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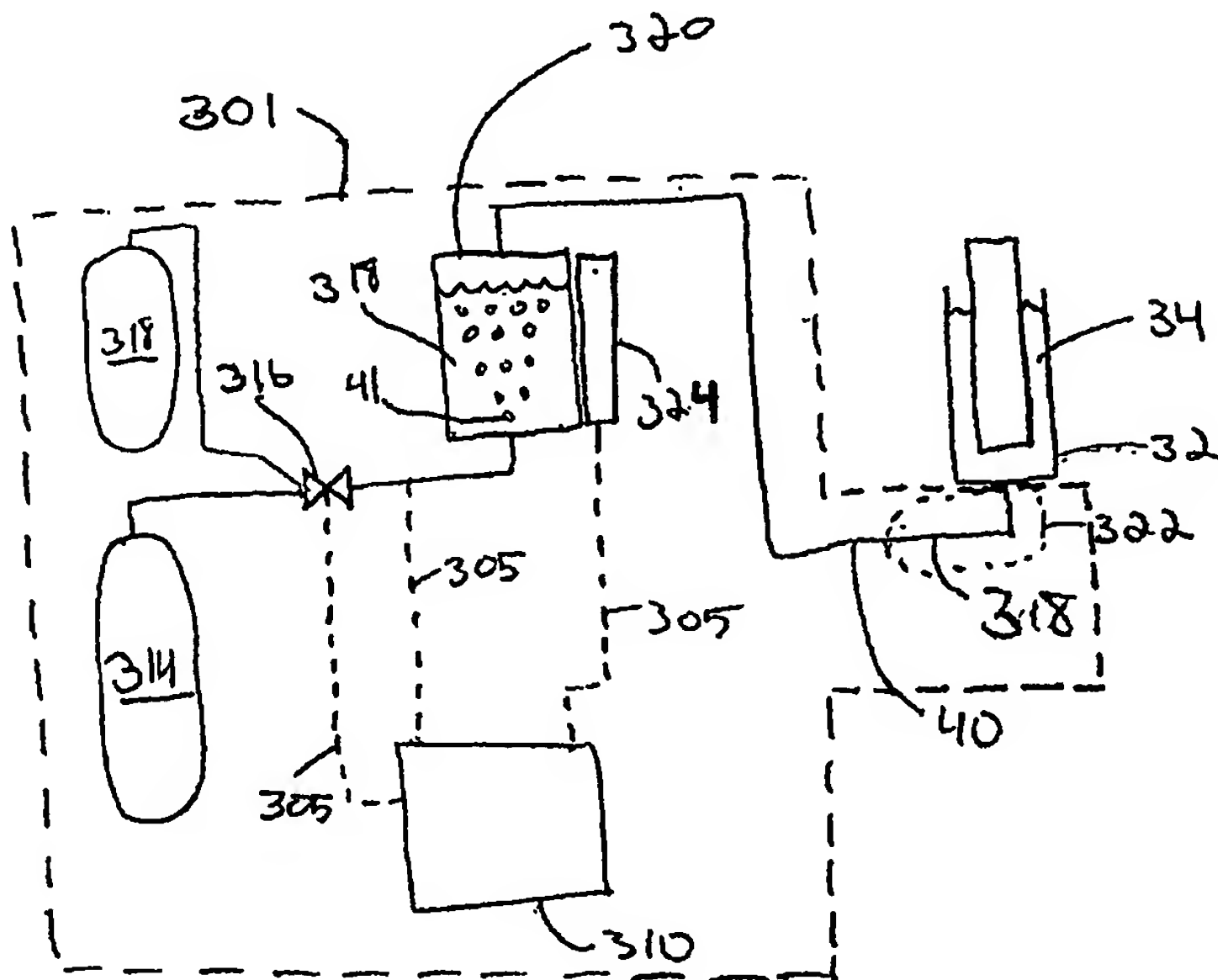
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- (54) Title:** AN ELECTROCHEMICAL SYSTEM AND METHODS FOR CONTROL THEREOF



- (57) Abstract:** The present invention relates to an electrochemical device. The device features an anode constructed of materials such that the device can be chemically recharged. In addition, the device is capable of switching between operating as a fuel cell or as a battery. In certain aspects of the invention, the device includes a liquid anode and is capable of operating at a temperature of less than 1000°C. Other aspects feature a control system and a fuel delivery system for the electrochemical system.





*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**AN ELECTROCHEMICAL SYSTEM AND METHODS FOR CONTROL  
THEREOF**

**Field**

5           The present invention relates to electrochemical systems including electrochemical devices capable of operation as either as fuel cells or batteries. The devices feature a chemically rechargeable anode, particularly where the anode comprises a liquid such as a metal or a metal alloy. Methods for controlling the electrochemical system are also disclosed.

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**Background**

          In a fuel cell comprising a solid oxide electrolyte, a cathode reduces oxygen to oxygen ions and an anode oxidizes a fuel accompanied by a release of electrons. The oxidized fuel combines with the oxygen ions to counteract a resulting flow of released  
15   electrons through an external circuit. The anode is not consumed during operation of the fuel cell. Theoretically, the fuel cell can operate as long as fuel is supplied to the anode.

          Electrical output depends on several factors, including the type of fuel used and the operational temperature, as well as the electrode and electrolyte components.  
20   To provide a high electrical output, new materials have been devised that can withstand high operational temperatures. Such high temperatures may not be practical for many applications, however. In addition, a combination of currently known materials results in a heavy device, which is not practical for some applications. Attempts to improve the performance of fuel cells include the discovery  
25   of new materials for anode, electrolyte and cathode components. Each device, however, is generally specific for a certain type of fuel.

          In a metal/air battery, a cathode reduces oxygen to oxygen ions in a similar manner to a fuel cell, but the anode itself oxidizes the process of which provides electrons which are released to an external circuit. Thus, the anode is consumed. For  
30   charge balance, the oxidized anode reacts with oxygen ions produced by the cathode.

The battery does not require fuel in order to generate electricity. The battery, however, has only a defined lifetime as determined by the lifetime of the anode.

Attempts have been made by others to combine the attributes of a fuel cell and a battery. For example, a device may comprise separate battery and fuel cell components, thus combining the storage capacity of a battery with the longevity of fuel cells. This arrangement, however, only adds to the weight of the device.

Much effort has been made, and continues to be made, to improve the performance of fuel cells and batteries, particularly for mobile applications where lightweight components and increased power output are essential.

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### **Summary of the Invention**

In one embodiment, the present invention is directed to an electrochemical system including an electrochemical device comprising an anode, a cathode, and an electrolyte. The electrochemical device is connectable to a fuel delivery system constructed and arranged to provide fuel to the electrochemical device, and is connectable to an oxygen delivery system constructed and arranged to provide oxygen to the electrochemical device. The electrochemical system further includes a control system, the control system including a sensor constructed and arranged to measure a property of an exhaust from the electrochemical device and produce a sensor signal representing the measured property and a controller constructed and arranged to receive the sensor signal from the sensor and provide a control signal to at least one of the fuel delivery system and the oxygen delivery system based, at least in part, on the sensor signal.

In another embodiment, the present invention is directed to an electrochemical system including an electrochemical device comprising an anode, a cathode, and an electrolyte, the electrochemical device connectable to a fuel delivery system constructed and arranged to provide fuel to the electrochemical device, and connectable to an oxygen delivery system constructed and arranged to provide oxygen to the electrochemical device. The electrochemical device also includes a control system including a sensor constructed and arranged to measure a property of the electrochemical device and produce a sensor signal representing the property and a

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controller constructed and arranged to receive the sensor signal from the sensor, correlate the sensor signal to a concentration of an anode species in the anode, and provide a control signal to at least one of the fuel delivery system and the oxygen delivery system based, at least in part, on the concentration of the anode species in the  
5 anode.

In another embodiment, the present invention is directed to a method of controlling an electrochemical system. The method includes measuring a property of an exhaust from an electrochemical device of the electrochemical system and controlling a function selected from the group consisting of the introduction of a fuel  
10 to the electrochemical device and the delivery of oxygen to the electrochemical device based, at least in part, upon the measured property of the exhaust of the electrochemical device.

In another embodiment, the present invention is directed to an electrochemical system including an electrochemical device, the electrochemical device including an  
15 anode, a cathode, and an electrolyte. The electrochemical device is connectable to a fuel delivery system constructed and arranged to provide fuel to the electrochemical device and connectable to an oxygen delivery system constructed and arranged to provide oxygen to the electrochemical device. The electrochemical system further includes a control system, including a sensor constructed and arranged to measure a  
20 property that is at least one of an open circuit voltage, a current, an AC impedance, a power output and a resistance of the electrochemical device and to produce a sensor signal representing the measured property. The control system further includes a controller constructed and arranged to receive the sensor signal from the sensor and to provide a control signal to at least one of the fuel delivery system and the oxygen  
25 delivery system based, at least in part, on the sensor signal.

In another embodiment, the present invention is directed to a method including measuring a property of an electrochemical system, correlating the measured property to a concentration of an anode species in an anode of an electrochemical device associated with the electrochemical system, and controlling the introduction of at least  
30 one of a fuel and oxygen to the electrochemical device based at least in part upon the concentration of the anode species in the anode of the electrochemical device.

In another embodiment, the present invention is directed to a method including measuring a concentration of an anode species in an anode of an electrochemical device associated with the electrochemical system, and controlling the introduction of at least one of a fuel and oxygen to the electrochemical device based at least in part upon the concentration of the anode species in the anode of the electrochemical device.

In another embodiment, the present invention is directed to an electrochemical system including an electrochemical device comprising an anode compartment constructed and arranged to at least partially contain a liquid anode, a fuel delivery system comprising a feed conduit fluidly connected to the anode compartment, and an anode flow prevention device associated with the feed conduit.

In another embodiment, the present invention is directed to an electrochemical system including an electrochemical device comprising an anode, a cathode and an electrolyte and a fuel other than hydrogen, carbon monoxide, methane or a mixture thereof deliverable to the anode. The electrochemical system is free of a fuel reformer.

In another embodiment, the present invention is directed to an electrochemical system including an electrochemical device comprising an anode, a cathode and an electrolyte; and a fuel including sulfur. The electrochemical system is free of a fuel desulfurizer.

In another embodiment, the present invention is directed to an electrochemical system including a first electrochemical device, an exhaust conduit fluidly connected to the first electrochemical device, and a second electrochemical device comprising a fuel delivery system in fluid communication with the exhaust conduit.

In another embodiment, the present invention is directed to an electrochemical system including an electrochemical device, a fuel delivery system connectable to the electrochemical device and arranged to provide fuel to the electrochemical device, and an anti-coking agent selected from the group consisting of water, oxygen, carbon monoxide, carbon dioxide, and combinations thereof, deliverable to the fuel delivery system.



In another embodiment, the present invention is directed to an electrochemical device including a fuel delivery system comprising a feed conduit connected to the electrochemical device and arranged to provide fuel to the electrochemical device and an anti-coking agent comprising a material selected from the group consisting of  
5 copper, nickel, platinum, oxygen, ruthenium, cerium, rhodium, osmium, aluminum, calcium, magnesium, sodium, other alkaline metals, other rare earth metals, and combinations thereof, the anti-coking agent associated with at least a portion of the feed conduit.

In another embodiment, the present invention is directed to an electrochemical  
10 system including an electrochemical device operable with a liquid anode and connectable to a fuel delivery system where the anode includes a cold zone associated with the fuel delivery system.

In another embodiment, the present invention is directed to a method of delivering fuel to an electrochemical device. The method includes flowing a fuel into  
15 a bottom portion of an anode compartment of the electrochemical device, the anode compartment having a bottom portion and a wall ascending from the bottom portion. The method further includes forming a bubble of the fuel on the bottom portion of the anode compartment until the bubble contacts a wall of the anode compartment and allowing the bubble to travel up the wall of the anode compartment.

20 In another embodiment, the present invention is directed to a method of delivering a fuel to an electrochemical device. The method includes flowing the fuel into the electrochemical device through a restriction sized and adapted to provide an upstream to downstream pressure ratio across the restriction of at least 1.1:1.

In another embodiment, the present invention may include a chemically  
25 rechargeable anode or liquid anode, an exhaust system, and a heat exchanger connected to the exhaust system.

In another embodiment, the present invention may include a chemically rechargeable anode or liquid anode, an exhaust system, and a combustion system connected to the exhaust system.

In another embodiment, the present invention may comprise a chemically rechargeable anode or liquid anode, an anode exhaust system, and a carbon dioxide separation system connected to the anode exhaust system.

Other advantages, novel features, and objects of the invention will become  
5 apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures is represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every  
10 component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

#### **Brief Description of the Drawings**

FIG. 1 shows a cross-sectional schematic diagram of a device of the present  
15 invention, highlighting the electrode and electrolyte components;

FIG. 2 shows a cross-sectional schematic diagram of a tubular device of the present invention, highlighting the electrode and electrolyte components;

FIG. 3 shows a cross-sectional schematic diagram of a tubular device of the present invention, highlighting the positioning of solid fuel positioned on the anode;

20 FIG. 4 shows a cross-sectional schematic diagram of a tubular device of the present invention, highlighting the positioning of an inlet positioned on one end of the anode, allowing exhaust to exit the other end of the anode;

FIG. 5 shows a cross-sectional schematic diagram of a planar stack of the present invention which utilizes liquid or gaseous fuels;

25 FIG. 6 shows a cross-sectional schematic diagram of a planar stack of the present invention which utilizes solid fuels;

FIG. 7 shows a three-dimensional schematic representation of the planar stack of FIG. 5;

30 FIG. 8 shows an interconnect positioned between two tubular devices of the present invention;



FIG. 9 shows a scheme of the various electrochemical processes that can be carried out by the anode of the present invention within a single device;

FIG. 10 is a schematic diagram of another embodiment of the present invention; and

5        FIG. 11 is a schematic diagram of another embodiment of the present invention.

### **Detailed Description**

#### **10    Chemically Rechargeable Anode Electrochemical Devices**

The present invention provides new electrochemical devices that display at least one or any combination of the following advantageous features: (1) a capability for chemical recharging; (2) simplified construction; (3) increased electrical output; and (4) a capability for providing a stack of electrochemical devices that afford low  
15    mechanical and thermal stresses. Certain aspects of the invention exploit the construction of an anodic material in conjunction with the use of different fuel types. The various embodiments of the present invention also provide novel methods for the generation of electricity.

One aspect of the present invention provides an electrochemical device. In  
20    one embodiment, electrochemical devices of the present invention are capable of converting chemical energy, via an electrochemical reaction, into electrical energy to produce an electrical output. Examples of electrochemical devices include a fuel cell and a battery. Other examples include an oxygen purifier and an oxygen sensor.

In one embodiment, the electrochemical device has a dual-mode capability in  
25    that the device can operate both as a fuel cell and as a battery. Thus, not only is the anode capable of oxidizing a fuel source and releasing electrons (e.g., as in a fuel cell), but the anode itself is capable of being oxidized with the release of electrons (e.g., as in a battery).

An advantage of this dual-mode capability can be illustrated by the following  
30    scenario. A typical prior art fuel cell can produce power so long as there is a supply of fuel. When the fuel supply is exhausted, the electrical output ceases almost

instantaneously. This situation can be disastrous especially when a fuel cell device is being used for variable load applications in which replacement fuel is not immediately available. To circumvent this problem, certain prior art fuel cell devices have been provided with a battery back-up. The addition of a separate battery, however, adds  
5 weight and complexity to the fuel cell device, which is undesirable especially for variable load applications.

The use of batteries as a sole source of power also has its disadvantages. In a typical battery, electrical power is generated at the expense of anode consumption, as the anode is consumed to release electrons. This anode consumption causes batteries  
10 to have a defined lifetime which is dictated, in large part, by the lifetime of the anode. To circumvent this problem, certain prior art electrically rechargeable batteries have been developed in which an input of electrons from an outside source reduces the consumed anode and restores the anode to its initial state. However, an external power source is required for electric recharging.

15 In contrast, the device of the present invention is capable of switching between "battery mode" and "fuel cell mode." For example, if the fuel supply is exhausted, the device can continue to generate electricity while operating in battery mode thereby eliminating the need for an external battery back-up. Furthermore, when the fuel supply is replenished the device in battery mode can switch back to fuel cell mode if  
20 so desired. These features will be discussed more fully below.

Another aspect of the invention provides an electrochemical device which comprises an anode constructed of a material such that the anode is a chemically rechargeable anode.

A "chemically rechargeable anode" refers to an anode capable of being  
25 recharged by the addition of a chemical reductant, as opposed to conventional electrically rechargeable devices. A "chemically rechargeable device" as used herein refers to a device comprising a chemically rechargeable anode. Prior to operation, the device of this aspect of the invention provides an anode having an initial oxidation state. When the device is operated in battery mode, at least a portion of the anode is  
30 consumed and electrons are released. A "consumed" anode or portion of the anode refers to an anode having a higher oxidation state than the initial oxidation state i.e.,

the anode is oxidized. Chemical recharging can be initiated by exposing the portion of the consumed anode to a chemical reductant resulting in that portion being reduced to a more reduced state, such as the initial oxidation state. Thus, it is the chemical reductant, not electricity (as in prior art devices), that, at least in part, recharges the anode. In one embodiment, the chemical reductant alone causes recharging of the anode. In another embodiment, a combination of chemical and electrical recharging results in restoration of the anode. An advantage of chemical recharging is the provision of the recharging species, (i.e., the chemical) located within the device itself. Thus no external recharging species is needed. This feature is particularly desired for use in areas where electrical power sources for electrical recharging may not be readily available.

Certain metal anodes are capable of existing in more than two oxidation states or in non-integral oxidation states. A metal or alloy comprises metals having a neutral charge. Certain metals can be oxidized to one or more oxidation states, any one of these states being of a sufficient electrochemical potential to oxidize the fuel. Conversely, if that metal is oxidized to its highest oxidation state, it can be reduced to more than one lower oxidation state (at least one having a higher oxidation state than neutral) where the anode is capable of functioning in any of these states. Alternatively, a metal oxide or mixed metal oxide may collectively oxidize fuel where metal ions are reduced by formal non-integer values.

In one embodiment, the chemical reductant is the fuel itself. An advantage of this embodiment can be illustrated with the previous scenario, in which the device is operating in battery mode. Upon depletion of the anode, the device can convert back to fuel cell mode where the fuel is consumed to produce electricity. In addition, the fuel can chemically recharge the oxidized anode to its initial state via a chemical reaction. A portion of the fuel reduces the anode and another portion of the fuel is oxidized to generate electricity. When the anode is restored (or a portion restored) to a reduced state, such as its initial state, the device regains its internal "battery back-up" for future emergency situations. The use of the fuel itself as a recharging source provides another advantage in that the device automatically contains the recharging source, thus eliminating the need to store additional chemicals into the device. In

other embodiment, however, it may be desired to incorporate another chemical reductant specifically for recharging the anode and having sufficient electrochemical activity to carry out this function.

In one embodiment, the chemically rechargeable device can be configured to allow recharging with electricity in addition to the chemical recharging capability. For certain anode materials and certain fuel types, it may be more feasible to recharge electrically if such an electrical power supply is readily available. For mobile applications, it is preferred that the anode is chemically rechargeable as well for the reasons described previously, e.g. eliminate need to carry a separate battery back-up for a lighter device.

In one embodiment, the anode comprises a liquid, preferably at temperatures for which the device is operable. A liquid is a material which exhibits flow properties. In one embodiment, a liquid is a material which exhibits a tendency to flow in response to an applied force under given operating conditions of temperature and pressure. Liquids generally have little or no tendency to spontaneously disperse. Preferably, materials which flow within a time scale that is not visually perceptible by the human eye are generally excluded from this definition.

One advantageous feature of a liquid anode is that fuel can be dispersed throughout the anode regardless of the physical state of the fuel, i.e., a gaseous, liquid or solid fuel can be dispersed throughout the anode. It is known that electrical output can be increased by increasing the surface area of an anode. Dispersing fuel throughout the anode allows maximization of the surface area exposed to the fuel. In addition, the liquid can be agitated by stirring or bubbling (or any other agitation methods) to help disperse the fuel throughout the liquid. In one embodiment, agitating the anode has further advantages where the anode undergoes oxide formation when consumed. The oxidized portion of the anode can be displaced with agitation to expose the unoxidized anode portions to the fuel. In contrast, a solid anode would form an oxidized portion at the anode/fuel interface, and the oxidized portion may block the fuel from accessing the anode. Additionally, a liquid anode reduces a need to machine the anode, as the anode can conform to any shape of casing used to house the device components. Where the electrolyte is a solid state

electrolyte, the anode can conform to the shape of the electrolyte, maximizing the surface area of contact between the anode and the electrolyte.

In one embodiment, the device is operable, with the anode in a liquid state, at a temperature of less than about 1500 °C, preferably at a temperature of less than about 1300 °C, more preferably less than about 1200 °C, even more preferably less than about 1000 °C, and even more preferably less than about 800 °C. By “operable”, it is meant that the device is able to generate electricity, either as a fuel cell or as a battery with the anode in a liquid state, and the anode may not necessarily be a liquid at room temperature. It is understood by those of ordinary skill in the art that anodic temperature can be controlled by selection of anode materials or in the case of an alloy, composition and percentages of the respective metal components, i.e., composition can affect a melting point of the anode. Other exemplary operating temperature ranges include a temperature between about 300 °C to about 1500 °C, between about 500 °C to about 1300 °C, between about 500 °C to about 1200 °C, between about 500 °C to about 1000 °C, between about 600 °C to about 1000 °C, between about 700 °C to about 1000 °C, between about 800 °C to about 1000 °C, between about 500 °C to about 900 °C, between about 500 °C to about 800 °C, and between about 600 °C to about 800 °C.

In one embodiment, the device is operable at a temperature at which any of the solid state components (e.g. a cathode or electrolyte) are not easily susceptible to cracking, i.e., the solid state components should maintain their structural integrity at the operating temperature of the device. In another embodiment, the device is operable at a temperature at which the cathode does not react with the electrolyte. In another embodiment, the device is operable at a temperature at which the anode comprises a liquid. One or any combination of these factors can be practiced independently or in combination, and those of ordinary skill in the art can balance these factors with the knowledge that increasing operational temperatures generally result in an increase in electrical output.

In one embodiment, the anode can be a pure liquid or can have solid and liquid components, so long as the anode as a whole exhibits liquid-like properties.

In one embodiment, the anode comprises a metal. The metal can be a pure metal or can comprise an alloy comprising two or more metals. Upon consumption of a portion of the anode, the portion of the anode is oxidized to form a metal oxide. A mixed metal oxide can be formed in the case where the anode is an alloy. In one  
5 embodiment, the metal has a standard reduction potential greater than -0.70 V versus the Standard Hydrogen Electrode (determined at room temperature). These values can be obtained from standard reference materials or measured by using methods known to those of ordinary skill in the art. In another embodiment, where the anode comprises more than one metal, all metals preferably have a standard reduction  
10 potential greater than -0.70V versus the Standard Hydrogen Electrode. Balancing the various electrochemical potential requirements can be determined by those of ordinary skill in the art. In certain embodiments, an alloy can be used where at least one of the metals does not have a standard reduction potential greater than -0.70V, but is included in the alloy to enhance flow properties, consistency, or other properties  
15 not related to electrochemical potential. In other embodiments, the anode can comprise a mixture of a metal and non-metals to enhance flow properties, consistency, or other properties not related to electrochemical potential.

In one embodiment, the anode comprises a conducting compound, preferably one that is molten at any of the operating temperatures disclosed herein.

20 In one embodiment, where the fuel is used to chemically recharge the anode, the oxidation potential of the fuel can dictate the anode composition, i.e., the oxidized state of the anode is of a sufficient electrochemical potential to oxidize the fuel.

In one embodiment, the anode is chemically rechargeable from the oxidized state. For example, where the oxidized state is a metal oxide or mixed metal oxide,  
25 the chemical recharging results in restoration (i.e. reduction) of the anode back to being a metal or metal alloy. In another embodiment, the chemical recharging results in reduction of the anode to an oxidation state capable of oxidizing the fuel.

In one embodiment, the anode comprises a metal or alloy comprising at least one of a transition metal, a main group metal, an alkaline metal, an alkaline earth  
30 metal, a lanthanide, an actinide and combinations thereof. In another embodiment, the anode comprises material such as copper, molybdenum, mercury, iridium,



palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, gadolinium, chromium nickel, iron, tungsten, cobalt, zinc, vanadium or combinations thereof. For example, the anode can comprise a pure metal such as antimony, indium, 5 tin, bismuth, mercury and lead. In another embodiment, the anode comprises an alloy of at least one element such as copper, molybdenum, mercury, iridium, palladium, antimony, rhenium, bismuth, platinum, silver, arsenic, rhodium, tellurium, selenium, osmium, gold, lead, germanium, tin, indium, thallium, cadmium, gadolinium, chromium nickel, iron, tungsten, vanadium, manganese, cobalt, zinc and 10 combinations thereof. Examples of alloys include 5% lead with remainder antimony, 5% platinum with remainder antimony, 5% copper with remainder indium, 20% lead, 10% silver, 40% indium, 5% copper.

In one aspect of the invention, the anode comprises a material that is different from the fuel composition, thus distinguishing the devices of the present invention 15 from metal/air batteries. Metal/air batteries are sometimes referred to as “fuel cells” because the lifetime of metal/air batteries can be increased by adding more anodic material. These batteries, however, do not provide the benefits of the devices of the present invention, as described herein. In one embodiment, the invention provides a method for energy conversion comprising the step of providing a battery and 20 supplying a fuel to an anode in the battery. The fuel is of a different material than the anode material. This embodiment allows the device to operate as a fuel cell and a battery. With other batteries, supplying a fuel that is of a different material than the anode material is an irrelevant step and serves no function.

In one aspect of the invention, the device comprises a source of fuel exposable 25 to the anode. “Exposable to the anode” refers to a capability for delivering fuel to the anode. For example, the fuel can be added directly to the anode. Alternatively, the fuel can be contained in a reservoir and can be deliverable to the anode, when needed, via a conduit leading from the reservoir to the anode. When the device is operating in battery mode, the fuel source can be shut off but remains exposable or capable of 30 being exposed to the anode at a later time when fuel cell mode is desired. Alternatively, the fuel can be in contact with the anode, i.e. dispersed throughout the

anode, positioned on a surface of the anode or otherwise contacted with the anode during operation and/or storage. In other embodiments, where the anode is a metal, the fuel can be in contact with metal oxide formed from the anode. The anode can be supplied with a new charge of fuel either continuously or periodically. This may be one viable arrangement for solid fuels. Depending on the physical state of the fuel (i.e., solid, liquid or gas), and other physical properties (powder, viscous liquid, etc.), those of ordinary skill in the art can readily construct a delivery mechanism to expose the fuel to the anode.

Examples of classes of fuels include a carbonaceous material; sulfur; a sulfur-containing organic compound such as thiophene, thiourea and thiophenol; a nitrogen-containing organic compound such as nylon and a protein; ammonia, hydrogen and mixtures thereof. Typically, the fuel selected for the device is mission dependent.

Examples of a fuel comprising a carbonaceous material include conductive carbon, graphite, quasi-graphite, coal, coke, charcoal, fullerene, buckminsterfullerene, carbon black, activated carbon, decolorizing carbon, a hydrocarbon, an oxygen-containing hydrocarbon, carbon monoxide, fats, oils, a wood product, a biomass and combinations thereof. Examples of a hydrocarbon fuel include saturated and unsaturated hydrocarbons, aliphatics, alicyclics, aromatics, and mixtures thereof. Other examples of a hydrocarbon fuel include gasoline, diesel, kerosene, methane, propane, butane, natural gas and mixtures thereof. Examples of oxygen-containing hydrocarbon fuels include alcohols which further include C<sub>1</sub>-C<sub>20</sub> alcohols and combinations thereof. Specific examples include methanol, ethanol, propanol, butanol and mixtures thereof. However, almost all oxygen-containing hydrocarbon fuels capable of being oxidized by the anode materials disclosed herein can be used so long as the fuel is not explosive or does not present any danger at operating temperatures.

Gaseous fuels such as hydrogen and SynGas (a mixture of hydrogen and carbon monoxide) can also be used in certain embodiments of the invention.

In another aspect of the invention, the electrochemical device is capable of operating with more than one type of fuel. The vast majority of prior art fuel cells are designed to operate with a specific fuel type, usually hydrogen and less often

methanol. This aspect of the invention makes it possible to capitalize on the benefits of different fuel types. For example, one type of fuel may provide a higher power output whereas another may provide a lower power output but affords lightweight properties. Enhanced performance may be achieved with one type of fuel, yet another  
5 type of fuel recharges the anode more efficiently. Other benefits for using different fuel types may be realized, for example, in situations where the price of one fuel type rises and economics dictate the use of a cheaper fuel. Environmental concerns may also be a deciding factor in changing the fuel type. Short term benefits may be realized, for example, in the situation where the supply of one fuel type is exhausted  
10 and only another fuel type is readily available.

In one embodiment, the device comprises a variable source of fuel for at least two different fuels. For example, the source of fuel can comprise at least two different reservoirs for two or more different fuels. Each fuel type can be accessed on demand individually, or in combination. In another embodiment, the source of fuel is  
15 capable of being interchanged with a different source of fuel. For example, an electrochemical device running on a gaseous fuel can run with a solid carbonaceous fuel dispersed throughout the anode. Those of ordinary skill in the art can readily devise a device comprising various delivery mechanisms.

Examples of electrochemical devices of the invention are illustrated in FIGs. 1  
20 and 2. FIG. 1 shows a cross-sectional schematic diagram of electrochemical device 2 having anode 4 in ionic communication with electrolyte 5. "Ionic communication" refers to a positioning and/or interconnecting of an electrode to an electrolyte to allow ions to migrate between the electrode and electrolyte. When anode 4 is in ionic communication with electrolyte 5, negative ions can migrate from electrolyte 5 to  
25 anode 4. An alternative arrangement (not shown here) can be provided where anode 4 is in ionic communication with electrolyte 5 even with an intervening layer of another material disposed between and contacting anode 4 and electrolyte 5. For example, a layer of a catalyst can be used as the intervening layer to increase the reaction rate between the oxidized fuel and oxygen anions. Electrolyte 5 is also in ionic  
30 communication with cathode 6 to allow negatively charged ions to migrate from cathode 6 to electrolyte 5. In the specific embodiment shown in FIG. 1, the electrodes

(anode 4 and cathode 6) and electrolyte 5 are shown as solid-state layers in which electrolyte layer 5 is disposed between and contacting anode layer 4 and cathode layer 6.

Leads (or current collectors) 8a and 8b are in electronic communication with anode 4 and cathode 6 respectively. "Electronic communication" refers to any pathway which provides for the transport of electricity. The electrochemical circuit is completed with external circuit 9 which electrically connect leads 8a and 8b. Circuit 9 is typically a metal wire or any material capable of conducting electricity. In one embodiment, lead 8a can comprise graphite and can serve the double function of collecting current and providing a fuel if at least partially submersed in anode 4.

Inlet 10 is a conduit for introducing fuel to the anode. Inlet 10 can be positioned, at least in part, within anode 4 to disperse fuel throughout the anode efficiently. Alternatively, inlet 10 does not have to contact anode 4 but can be positioned at a minimally close distance to allow all the fuel released through inlet 10 to contact anode 4. Inlet 10 can be further connected to a reservoir (not shown) that comprises a source of fuel with or without the use of a conduit. A variety of reservoirs have been or can be developed for the delivery of solid, gaseous or liquid fuel. For example, the reservoir can comprise a pressurized tank of gaseous or liquid fuel. It is not necessary to provide liquid fuels in pressurized form although pressurization advantageously compacts the fuel volume. Solid fuel can be provided as a powder or other deliverable forms poured, sprayed or otherwise distributed from a reservoir in pure form or as a slurry. Optionally other mechanisms can be attached which forces the fuel from the reservoir through a conduit and through inlet 10.

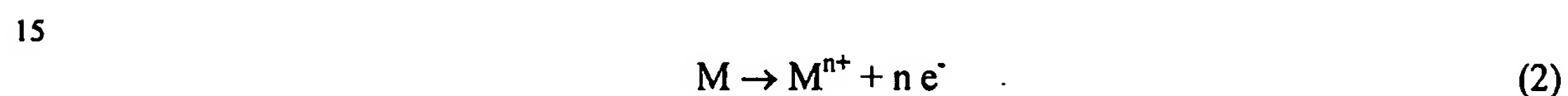
Not shown in FIG. 1 is a casing for containing and/or protecting device 2. The casing is preferably constructed of a material that can withstand the desired operating temperature. Also not shown in FIG. 1 is a housing to isolate the anode from atmospheric oxygen, and this housing can be the same or different as the casing that contains device 2. In these embodiments, a conduit which penetrates the casing and/or housing can be provided for delivering the oxygen-containing flow 7 to cathode 6. The device can further comprise another conduit to release waste products, such as gases or liquids, from the casing and/or housing.

The cathode ionizes oxygen to oxygen ions as represented by the electrochemical half reaction shown in eq. 1:



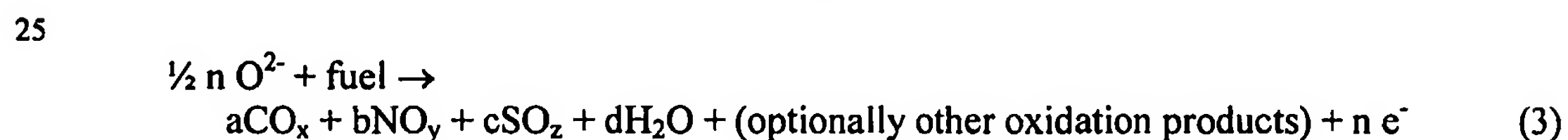
5 This ionization occurs when the device operates in battery or fuel cell mode. The cathode can be exposed to air, pure oxygen or any oxygen-containing gas 7, at atmospheric pressures or greater. Alternatively, the device can include an inlet to expose cathode 6 to the oxygen-containing gas 7. Typically, oxygen is reduced at an  
10 interface between cathode 6 and the oxygen-containing gas 7. Cathode 6 preferably comprises a material which allows oxygen ions to migrate through cathode 6 and access electrolyte 5.

When the fuel cell operates in battery mode, the anode itself is consumed as represented by the electrochemical half reaction of eq. 2:



where M represents a metal or metal alloy (and accordingly,  $\text{M}^{n+}$  represents an oxidized metal or alloy), “e<sup>-</sup>” denotes an electron, and n is greater than or equal to 1,  
20 depending on the metal or metal alloy.  $\text{M}^{n+}$  is typically present as a metal oxide (or mixed metal oxide). As described previously, the portion of the anode that is oxidized, as shown in eq. 2, forms an oxidized portion on or within the anode.

When the device is in fuel cell mode, a variety of reactions can occur. The fuel is oxidized at the anode, thereby releasing electrons, as represented in eq. 3:

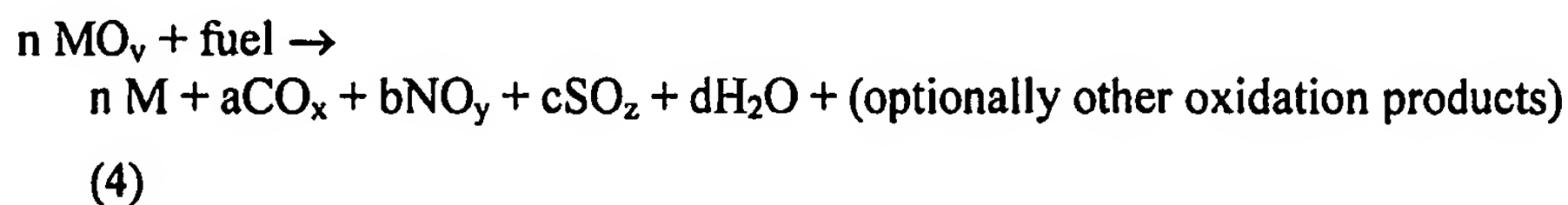


30 The oxygen anions shown in eq. 3 are, for the most part, supplied by the cathode reaction of eq. (1). Eq. 3 is intended to represent some of the various possible oxidation products. The coefficients a, b, c, d, x, y, and z can be the same or different and each are greater than or equal to zero and their values depend on the type of fuel used, and at least one of a, b, c, d, x, y, and z will be greater than zero. The coefficient “n” is greater than 0. The fuel may comprise a combination of “a” carbon

atoms and/or “b” nitrogen atoms and/or “c” sulfur atoms and/or d hydrogen atoms, etc. For example,  $\text{CO}_x$  can represent  $\text{CO}_2$ , CO or a mixture thereof. If hydrogen is the fuel, water is the sole oxidation product. Not all possible oxidation products are represented by eq. 3 and depending on the composition of the fuel, those of ordinary skill in the art can determine the resulting oxidation product. Thus, a net reaction of the anode in fuel cell mode involves oxidation of the fuel with no consumption of the anode.

Without wishing to be bound by any theory, the recharging of the anode by the fuel is represented by eq. (4).

10



15

The reaction of eq. (4) is similar to that of eq. (3), except the oxygen anions are provided, at least in part, by the metal or mixed metal oxide, “ $\text{MO}_v$ ” where “v” is greater than 0.

20

In one embodiment, the device is capable of electrical output of at least about 10 mWatt/cm<sup>2</sup>, preferably at least about 50 mWatt/cm<sup>2</sup>, preferably at least about 100 mWatt/cm<sup>2</sup>, even more preferably at least about 200 mWatt/cm<sup>2</sup>, even more preferably at least about 300 mWatt/cm<sup>2</sup>, and even more preferably at least about 500 mWatt/cm<sup>2</sup>.

25

In one embodiment, the cathode is a solid state cathode. Examples of solid state cathodes include a metal oxide and a mixed metal oxide. Specific examples include tin-doped  $\text{In}_2\text{O}_3$ , aluminum-doped zinc oxide and zirconium-doped zinc oxide. Another example of a solid state cathode is a perovskite-type oxide having a general structure of  $\text{ABO}_3$ , where “A” and “B” represent two cation sites in a cubic crystal lattice. A specific example of a perovskite-type oxide has a structure  $\text{La}_x\text{Mn}_y\text{A}_a\text{B}_b\text{C}_c\text{O}_d$  where A is an alkaline earth metal, B is selected from the group consisting of scandium, yttrium and a lanthanide metal, C is selected from the group consisting of titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc,

30



zirconium, hafnium, aluminum and antimony, x is from 0 to about 1.05, y is from 0 to about 1, a is from 0 to about 0.5, b is from 0 to about 0.5, c is from 0 to about 0.5 and d is between about 1 and about 5, and at least one of x, y, a, b and c is greater than zero. More specific examples of perovskite-type oxides include  $\text{LaMnO}_3$ ,

5  $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ ,  $\text{La}_{0.84}\text{Ca}_{0.16}\text{MnO}_3$ ,  $\text{La}_{0.84}\text{Ba}_{0.16}\text{MnO}_3$ ,  $\text{La}_{0.65}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_3$ ,  $\text{La}_{0.79}\text{Sr}_{0.16}\text{Mn}_{0.85}\text{Co}_{0.15}\text{O}_3$ ,  $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$ ,  $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ,  $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_3$ ,  $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ ,  $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$ ,  $\text{La}_{0.6}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Al}_{0.2}\text{O}_3$ ,  $\text{La}_{0.84}\text{Sc}_{0.16}\text{MnO}_3$ ,  $\text{La}_{0.84}\text{Y}_{0.16}\text{MnO}_3$ ,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ ,  $\text{LaCoO}_3$ ,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$  and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ .

10 Other examples of solid state cathodes include  $\text{LaCoO}_3$ ,  $\text{LaFeO}_3$ ,  $\text{LaCrO}_3$ , and a  $\text{LaMnO}_3$ -based perovskite oxide cathode, such as  $\text{La}_{0.75}\text{Sr}_{0.25}\text{CrO}_3$ ,  $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.9}\text{CrO}_3$ ,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ ,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  or  $\text{Ln}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ , where Ln can be any one of La, Pr, Nd, Sm, or Gd.

Alternatively, the cathode can comprise a metal. Exemplary metal cathodes  
15 include platinum, palladium, gold, silver, copper, rhodium and combinations thereof.

The electrolyte allows conduction of ions between the cathode and anode. The electrolyte allows migration of oxygen ions from the cathode to the anode. In one embodiment, the electrolyte is a solid state electrolyte. Example solid state electrolytes include a metal oxide and mixed metal oxides.

20 An example of a solid state electrolyte is an electrolyte having a formula  $(\text{ZrO}_2)(\text{HfO}_2)_a(\text{TiO}_2)_b(\text{Al}_2\text{O}_3)_c(\text{Y}_2\text{O}_3)_d(\text{M}_x\text{O}_y)_e$  where a is from 0 to about 0.2, b is from 0 to about 0.5 c is from 0 to about 0.5, d is from 0 to about 0.5, x is greater than 0 and less than or equal to 2, y is greater than 0 and less than or equal to 3, e is from 0 to about 0.5, and M is selected from the group consisting of calcium, magnesium,  
25 manganese, iron, cobalt, nickel, copper, and zinc. More specifically, examples of solid state electrolytes include  $(\text{ZrO}_2)$ ,  $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}$ ,  $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ ,  $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.05}$ ,  $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}(\text{TiO}_2)_{0.10}$ ,  $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}(\text{Al}_2\text{O}_3)_{0.10}$ ,  $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{Fe}_2\text{O}_3)_{0.05}$ ,  $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{CoO})_{0.05}$ ,  $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{ZnO})_{0.05}$ ,  $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{NiO})_{0.05}$ ,  
30  $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{CuO})_{0.05}$ ,  $(\text{ZrO}_2)(\text{Y}_2\text{O}_3)_{0.08}(\text{MnO})_{0.05}$  and  $\text{ZrO}_2\text{CaO}$ .

Other examples of solid state electrolytes include a  $\text{CeO}_2$ -based perovskite, such as  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$  or  $\text{Ce}_{1-x}\text{Gd}_x\text{O}_2$  where  $x$  is no more than about 0.5; lanthanum-doped ceria, such as  $(\text{CeO})_{1-n}(\text{LaO}_5)_n$  where  $n$  is from about 0.01 to about 0.2; a  $\text{LaGaO}_3$ -based perovskite oxide, such as  $\text{La}_{1-x}\text{A}_x\text{Ga}_{1-y}\text{B}_y\text{O}_3$  where  $A$  can be Sr or Ca,   
 5 B can be Mg, Fe, Co and  $x$  is from about 0.1 to about 0.5 and  $y$  is from about 0.1 to about 0.5 (e.g.  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ ); a  $\text{PrGaO}_3$ -based perovskite oxide electrolyte, such as  $\text{Pr}_{0.93}\text{Sr}_{0.07}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3$  or  $\text{Pr}_{0.93}\text{Ca}_{0.07}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3$ ; and a  $\text{Ba}_2\text{In}_2\text{O}_5$ -based perovskite oxide electrolyte, such as  $\text{Ba}_2(\text{In}_{1-x}\text{Ga}_x)_2\text{O}_5$  or  $(\text{Ba}_{1-x}\text{La}_x)\text{In}_2\text{O}_5$ , where  $x$  is from about 0.2 to about 0.5.

10 In one embodiment, the electrochemical device is a solid-state device which comprises solid-state cathode and electrolyte components as described previously. Preferably, the anode is a liquid as described previously.

In one embodiment, the device provides an electrolyte having small thicknesses. A small thickness provides at least one of many advantageous features:   
 15 (1) efficient migration of ions; (2) provision of the oxygen-containing gas at relatively low pressures; and (3) facile design of miniature devices. In one embodiment, the electrolyte has a thickness of less than about 200  $\mu\text{m}$ , and more preferably less than about 100  $\mu\text{m}$ .

FIG. 1 shows a cross-section of a device in which each component can be   
 20 provided as a flat layer or a shaped layer. For example, FIG. 1 can also represent a cross-section of a shaped device such as a tubular device. By "shaped device" it is meant that the electrode-electrolyte configuration can be provided as any shape besides a flat layer, as known to those of ordinary skill in the art.

FIG. 2 shows a schematic cross-section of one type of shaped layer, i.e.   
 25 tubular device 12. Device 12 of FIG. 2 has similar components as device 2 of FIG. 1. In FIG. 2, anode 14 is centrally positioned within and enclosed by electrolyte 15. Encircling electrolyte 15 is cathode layer 16. Leads 18a and 18b contact anode 14 and cathode 16 respectively. Inlet 20, for introducing gaseous or liquid fuels if applicable, is shown submersed in the anode but can be positioned anywhere that   
 30 allows the fuel to be exposable to anode 14. Optionally, cathode layer 16 can be positioned within a casing to protect cathode layer 16 from breakage, as cathode layer

16 is typically provided as a thin layer. The casing may be sufficiently porous to allow oxygen to access cathode layer 16. Alternatively, device 12 can further comprise one or more conduits (not shown) to provide an oxygen-containing gas flow 17 to the cathode, or for removing exhaust from the device.

5 Another aspect of the present invention provides a housing for the anode comprising a solid-state electrolyte material. This feature provides an efficient design for an electrochemical device as the solid-state electrolyte serves two functions: (1) as a medium for the transport of ions to and from the electrodes; and (2) for containing a liquid anode. Design efficiency is advantageous, particularly when  
10 stacks of electrochemical devices are employed. In this aspect, a separate housing is eliminating, thus reducing cost of materials and resulting in a more lightweight device. The electrolyte housing can be constructed solely of electrolyte material, or partially of electrolyte material. Ideally, the housing should comprise enough electrolyte material to span a dimension of the anode, such as in FIG. 2 (electrolyte  
15 makes up essentially the entire housing) or FIGs. 3 and 4 (electrolyte makes up wall 25 only). Of course, the electrolyte material can be of any dimension, depending on the electrical output and/or economic requirements. Generally, efficient device design results from maximizing the surface area which provides ionic communication between the electrode/electrolyte components.

20 Alternatively, the housing can comprise a mixture of electrolyte and non-electrolyte materials. Preferred non-electrolyte materials in this mixture have thermal expansion coefficients substantially similar to the electrolyte material. In one embodiment, the thermal expansion coefficients of the electrolyte and non-electrolyte materials differ by less than about 30% at a temperature of less than about 1500°C,  
25 preferably less than about 20% and more preferably less than about 10%. Example non-electrolyte materials that can be included in this mixture include  $\alpha\text{-Al}_2\text{O}_3$ .

In one embodiment, an electrolyte housing is surrounded and in ionic communication with a cathode material. In this embodiment, the cathode conforms to the shape of the electrolyte, or at least to the dimension of the electrolyte which spans  
30 a dimension of the anode. FIG. 2 shows cathode 16 in conforming contact with electrolyte 15 which also functions as a housing for the anode. FIG. 3 shows another

embodiment, where cathode 26 only surrounds the walls of electrolyte 25, leaving base 29 free of contact with cathode material.

Another advantageous feature of a liquid anode in certain embodiments involves the ability of the anode to act as a sealant precursor to seal a flaw in the device. In this embodiment, the device is “self-repairing”, and does not require any active human intervention for the repair. For example, when a solid state electrolyte develops a crack or other flaw, a liquid metal anode can flow to substantially cover and/or substantially fill the crack. Subsequently, the anode can react with oxygen to form a metal oxide (or mixed metal oxide in the case where the anode is an alloy). The resulting oxide formed substantially conforms to the crack due to the flow properties of the initially liquid anode. Even though the present device minimizes thermal and mechanical stresses due to the liquid properties of the anode, the self-repairing capability helps to ensure the integrity of the device, particularly when repair is not feasible, e.g. during operation of the system.

FIGs. 3 and 4 display various methods of exposing an anode to a source of fuel. FIG. 3 shows a cross-sectional schematic diagram of a tubular device 22 having electrolyte 25 in ionic communication with anode 24 and cathode 26. Base 29 can be of the same material as electrolyte 25, or of a different material and the connection between electrolyte 25 and base 29 can be integral or non-integral. Lead 28a (which can comprise a graphite material) is submersed in anode 24 and is electrically connected to lead 28b which is in electronic communication with cathode 26. Fuel 23 is shown positioned on top of anode 24 and can either be consumed in this manner or can be dispersed throughout the anode. This arrangement is useful in the situation where the fuel is not easily transferred from an inlet, such as in the case of certain solid fuels. Optionally, the device can further comprise a mechanism for urging fuel 23 towards the anode as fuel 23 is consumed. An urging mechanism allows maximum contact surface area between fuel 23 and anode 24. Examples of urging mechanisms include various mechanical devices, such as a spring, a clamp, a rod or a diaphragm, or other urging mechanisms known to those of ordinary skill in the art. Mixing or agitation can also accomplish the urging.

FIG. 4 shows a cross-sectional schematic diagram of tubular device 32, featuring another position of inlet 40 with respect to device 32. Device 32 comprises electrolyte 35 in ionic communication with anode 34 and cathode 36. Base 39 can be of the same or a different material as electrolyte 35 and the connection between electrolyte 35 and base 39 can be integral or non-integral. Lead 38a is partially submersed in anode 34 and does not extend all the way to base 39. Inlet 40 penetrates through base 39 to the extent that a space exists between inlet 40 and lead 38a. Upon release of fuel 41 into anode 34 through inlet 40, the fuel can be readily dispersed throughout a maximum portion of anode 34. Another advantage to this arrangement is that any waste products will naturally travel to an aperture opposite, or at a distance from inlet 40, for example, areas 42 in which anode 34 contacts the atmosphere. Alternatively, the device of the present invention can further comprise an exhaust conduit to remove any waste from the device.

Certain prior art devices require operating temperatures of greater than 1000°C. It is generally desired to lower these operating temperatures to minimize thermal energy provided to the device. Exceedingly high temperatures may also lead to electrolyte or cathode cracking or the formation of other flaws in the device. In addition, rapid start-up heating times provides an advantage in the situation where electrical power is required quickly. The higher the operating temperature, however, the greater the time needed for start-up heating of the device.

Thus, another aspect of the present invention provides an electrochemical device comprising an anode comprising a liquid at a temperature of no more than about 1000°C. The ability to provide a liquid anode at lower operating temperatures, such as a temperature below 1000°C, reduces a temperature range required for start-up heating. In addition to reducing start-up heating times, lower temperatures afford a more hospitable environment for maintaining the integrity of an interface between different components such as the anode/electrolyte or electrolyte/cathode components.

Another aspect of the present invention provides an electrochemical device comprising an anode and an intermittent fuel source deliverable to the anode to produce a continuous electrical output from the device. "Intermittent fuel source" refers to any fuel source arranged to allow cessation between a period of delivery of



the fuel to the anode. In one embodiment, the cessation can be periodic or random. Cessation can be a multiple occurrence or a one-time occurrence. It is a feature of this aspect of the invention that even with this cessation of fuel delivery a continuous electrical output is produced. In one embodiment, an intermittent fuel source can be  
5 used when the device is switched from fuel cell mode to battery mode where fuel is not delivered to the anode. When fuel is supplied to the device, electricity can be generated via fuel cell operation. Ceasing delivery of fuel to the anode causes the device to switch to battery mode for continuous generation of electricity. An electrical device can be manufactured, using the methods and materials described  
10 herein, to derive power continuously while experiencing minimal or almost no shut down time as the electrical device switches between fuel cell and battery modes. During intermittent fuel delivery, the fuel source can also be changed or replenished.

In one embodiment, switching from fuel cell mode to battery mode and vice versa occurs automatically. For example, the device of the present invention can  
15 operate in fuel cell mode until the fuel is exhausted. Automatic switching is demonstrated when the anode begins to oxidize, thereby releasing electrons, i.e., the device automatically operates in battery mode. In one embodiment, the switching can occur by simply shutting off fuel delivery to the anode or turning on the fuel source. Alternatively, a switch can be constructed which stops/starts introduction of fuel to  
20 the anode. Other switching mechanisms can be readily envisioned by those of ordinary skill in the art.

In one embodiment, the device can operate simultaneously in fuel cell and battery mode. In this embodiment, fuel consumption and fuel oxidation by the anode occur simultaneously. This may occur when fuel is supplied to the anode at a low  
25 flow rate and/or in low amounts. Alternatively, simultaneous fuel cell and battery operation may inherently occur when fuel is supplied to the device. Switching between fuel cell and battery mode can occur, not as a sharp on/off event, but gradually as the amount of fuel supplied to the anode is increased or decreased.

Another aspect of the invention provides an electrochemical device  
30 comprising an anode and a source of fuel exposable to the anode. The anode is constructed of a material such that the device is capable of producing electricity by



using the anode (the anode is included in a circuit in which the electricity is produced) in both the presence of fuel without anode consumption (or without net anode consumption, i.e., less anode is consumed than regenerated) and in the absence of fuel. In one embodiment, a device “capable of producing electricity involving the anode in the presence of fuel without anode consumption” refers to generation of electricity via fuel cell operation. Conversely, the same anode can deliver electrons to the device without exposure to fuel in which the anode is consumed, such as when the device operates in battery mode. In one embodiment, the electrochemical device is a fuel cell/battery hybrid capable of operating in either fuel cell or battery mode, while producing a continuous electrical output.

Another aspect of the present invention provides a stack of electrochemical devices. Electrical output can be multiplied by supplying a number of devices as described above into one system. For variable load applications, it is usually desired that the stack be lightweight and capable of miniaturization. FIG. 5 shows an example of a stack 100 of planar electrochemical devices. Each device in stack 100 comprises an anode 104 in ionic communication with electrolyte 105. Electrolyte 105 in turn is in ionic communication with cathode 106. Stack 100 further includes an inlet 110 for liquid or gaseous fuel to be provided to each device via guide 111. Inlet 112 allows oxygen to be supplied via guide 113 to each cathode 106. Conduit 114 and outlet 115 serve to remove any exhaust gases from stack 100. The multi-device system is positioned within casing 102. Stack 100 further includes preheating chamber 116 to heat each device to an operational temperature.

In this aspect, a liquid anode is particularly advantageous due to its moldable properties. The liquid can function as a seal between each device. Moreover, the liquid provides a soft contact between the liquid anode and the adjacent device to reduce mechanical and thermal stresses between the devices.

FIG. 5 shows each device in the stack arranged and positioned in a repeat array to arrange identical components in the same orientation. This arrangement may relieve stresses on each device, particularly taking advantage of the soft contact provided by the anode. A variety of arrangements of the devices in the stack can be envisioned to maximize the number of devices that receive fuel from guide 111.

In other embodiments, the devices in the stack can be arranged in series, parallel or can comprise a series-parallel configuration.

The stack need not necessarily be arranged in planar configuration and can be arranged in any array, e.g. such as a rectangular or hexagonal array.

5        Another advantageous feature of the liquid anode is that by positioning a liquid adjacent a solid component, a non-permanent seal is formed. This non-permanent attachment removes a need to add further components to hold each device adjacent to each other such as adhesives or mechanical attachments. In one embodiment, the casing can provide a series of slots. Each device can simply be  
10        guided through the slots to provide the stack. In the event of a malfunction of an individual device, the malfunctioning device can be removed and easily replaced with a new device. For other prior art devices, when one individual device malfunctions, either the permanent seal would have to be broken to replace the individual device or the entire stack will need to be repaired. Of course, other embodiments may provide a  
15        permanent seal in addition, depending on the application.

FIG. 6 shows an alternative example of a stack utilizing solid fuel. FIG. 6 shows stack 120 having anode 124 positioned adjacent electrolyte 125 which in turn is positioned adjacent cathode 126. Inlet 132 directs oxygen to individual devices via conduit 133. Solid fuel 130 is positioned within anode 124. Solid fuel 130 can also  
20        act as a lead to collect electricity from the anode. Each device can be positioned within casing 122. Casing 122 can further comprise inlets to provide more solid fuel to the device, or a reservoir for additional solid fuel sources. Each device in stack 120 can be tubular or planar.

In one embodiment, the stack can further comprise an interconnect positioned  
25        adjacent the anode of a first device and the cathode of the second device. An interconnect has an air flow pattern to allow oxygen flow in or out of the stack. In addition, an interconnect can convey electrical currents and/or thermal energy away from each device. Preferably, the interconnect has sufficient electrical conductivity and thermal conductivity to achieve this function. To reduce the likelihood of  
30        forming cracks in the device, it is preferred that the interconnect and cathode have similar thermal coefficients. In one embodiment, respective thermal expansion

coefficients of the cathode and interconnect differ by less than about 30% at a temperature of less than about 1500°C, preferably less than about 20% and more preferably less than about 10%. In one embodiment, the interconnect comprises substantially the same material as the cathode, and thus the respective thermal  
5 coefficients would theoretically differ by about 0%.

Referring back to FIGs. 5 and 6, interconnects 107 and 127 are shown as being positioned adjacent cathodes 106 and 126, respectively, and the adjacent anodes. FIG. 7 shows a close-up of a stack of FIG. 5. Stack 100 features interconnect 107 positioned adjacent cathode 106. Interconnect 107 is also positioned adjacent an  
10 anode.

FIG. 8 shows another exemplary arrangement for connecting two tubular devices of the invention together to form a stack via an interconnect. In FIG. 8, stack 140 comprises individual units each comprising anodes 144a and 144b positioned adjacent and within electrolyte layers 145a and 145b, respectively. Cathodes 146a  
15 and 146b are provided as a layer which coats at least a portion of electrolytes 145a and 145b. Fuel sources 150a and 150b can be positioned adjacent anodes 144a and 144b. Where the fuel is a solid fuel, fuel sources 150a and 150b can comprise a solid rod, such as graphite. In addition, the solid rod can also function as a current collector. Alternatively, for liquid, gaseous or solid powder fuels, fuel sources 150a  
20 and 150b can comprise an inlet positioned within or near anodes 144a and 144b to guide and disperse the fuels throughout anodes 144a and 144b. In any situation, a lead would be required to be positioned in anode 144b and lead 154 can be positioned adjacent cathode 146a. Interconnect 152 is positioned adjacent electrolyte layer 145a and cathode layer 146b. To allow interconnect 152 to contact anode 144a, holes can  
25 be provided in a portion of electrolyte 145a which contacts interconnect 152. Thus, the anode 144a can flow through the holes to eventually contact interconnect 152. FIG. 8 shows tubular arrangements, but those of ordinary skill in the art can readily design an analogous planar device, in light of the description provided herein.

As discussed previously, typical fuel cell interconnects include a gas flow  
30 pattern. In one embodiment, an interconnect of the present invention is free of a gas flow pattern, particularly when used with a liquid anode. Because fuel and waste are

dispersible throughout the anode and can enter or exit each device via the liquid anode, a gas flow pattern is not essential for the interconnect of the present invention. It is understood that other fuel types may still require an interconnect with a gas flow pattern for enhanced device performance.

5 As discussed previously, the interconnect is positioned adjacent a liquid anode, thus reducing many problems associated with thermal coefficients mismatches that may arise as the device is heated to high temperatures. Accordingly, it has been discovered that such moldability of the liquid anode allows the interconnect to have much thinner dimensions than many prior art interconnects. This allows interconnects  
10 to be more lightweight and less expensive and these benefits can be extended to the manufacturer of the device.

Thus, the interconnect of the present invention can provide at least one of the following advantages: (1) a reduction in weight by at least 20%, preferably by at least 30% and more preferably by at least 40% compared to prior art interconnects; (2)  
15 elimination of intricate, machined gas flow patterns, which reduces the cost and manufacture time; and (3) rapid and repeated start-up heating of the stack due to the minimal thermal and mechanical stresses resulting from contact with adjacent anode and cathode materials.

FIG. 9 shows a schematic diagram summarizing various electrochemical  
20 processes that can be carried out by the anode of the present invention. In FIG. 9, anode 200 is represented as "M" in which anode 200 comprises a metal or metal alloy. Eq. 202 of FIG. 9 schematically represents anode 200 functioning as a battery. In eq. 202, anode 200 combines with "y" moles of  $O^{2-}$  produced from a cathode. In battery mode, anode 200 releases electrons resulting in the oxidation of M to form a  
25 metal or mixed metal oxide,  $M_xO_y$ . Eq. 203 schematically shows the chemical rechargeability of the anode which, in the presence of fuel, is reduced back to metal anode 200. In eq. 203, it is the metal oxide that combines with the fuel to produce fuel oxidation products. " $M_xO_y$ " should be of a sufficient electrochemical potential to be reduced by the fuel. Without wishing to be bound by any theory, the combination  
30 of eqs. 202 and 203 schematically illustrates the process undergone by anode 200 when operating in fuel cell mode, in which there is no net consumption of anode.

Thus, FIG. 9 shows the capability of anode 200 to: (1) be oxidized in the absence of a fuel and produce electricity, as shown in eq. 202; (2) regenerate from a corresponding metal oxide, as shown in eq. 203; and (3) oxidize fuel with no net consumption of the anode, as represented by eqs. 202 and 203.

5           Accordingly, another aspect of the present invention provides a method for energy conversion. The method involves providing an electrochemical device comprising an anode, such as any anode described herein. The method also involves causing electricity to be produced when the anode is exposed to a fuel, such that electricity is produced without anode consumption (i.e. anode acts as a catalyst). In  
10 one embodiment, this step is exemplified by eqs. 202 and 203 of FIG. 9. The method also involves causing electricity to be produced in the device in the absence of fuel provided to the anode. This step is distinguished from other devices which provide a back-up battery source having another anode, in the event the fuel supply is exhausted. The present invention allows the same anode to cause electricity to be  
15 produced in the presence of a fuel (i.e., when in fuel cell mode) and to cause electricity to be produced in the absence of the fuel. In one embodiment, this step is exemplified by eq. 202 of FIG. 9.

          In one embodiment, either step of causing electricity to be produced in the presence or absence of a fuel involves providing an electrolyte in ionic  
20 communication with the anode and a cathode in ionic communication with the electrolyte. These steps can also involve directing an oxygen-containing gas flow to the cathode. In one embodiment, the causing steps can also include heating the device from a temperature of about 300 °C to about 1500 °C, or within other temperature ranges as described previously. Preferably, the chosen temperature range involves  
25 producing the anode in a liquid state.

          In the embodiment where electricity is produced in the absence of the fuel, the anode is typically consumed. Thus, in one embodiment, the method further comprises providing fuel to the anode to chemically recharge the anode. In one embodiment, this step is exemplified by eq. 203 of FIG. 9.

30           Another aspect of the present invention provides a method for energy conversion. The method involves providing an anode and delivering a fuel to the



anode intermittently while producing a continuous electrical output by using the anode. As described previously, “intermittently” can involve any cessation of fuel delivery to the anode. “Producing a continuous electrical output by using the anode” refers to use of the anode continuously, even though fuel is provided to the anode  
5 intermittently. A device comprising a fuel cell and a separate battery back-up is excluded from this aspect of the invention, because when fuel is supplied, the anode of the fuel cell is used to produce electricity. When fuel delivery ceases in favor of the battery backup, the anode of the battery and not the anode of the fuel cell, is used to produce electricity. Thus, the anode of the fuel cell is not used continuously in the  
10 continuous production of electricity.

Another aspect of the present invention provides a method involving providing an anode and causing a portion of the anode to be oxidized such that electricity is produced. In one embodiment, this causing step occurs when the anode is operated as a battery, as exemplified by eq. 202 of FIG. 9. The “portion of the anode” is  
15 described as follows. Initially, the portion of the anode that is immediately adjacent the electrolyte is oxidized, as this portion represents the shortest diffusion pathway by which oxygen ions released by the cathode can access the anode. As device operation continues, this oxidized portion grows from the anode/electrolyte interface toward the bulk of the anode, as the anode continues to be consumed.

At any stage of anode consumption, either initially or when the entire anode has been consumed (i.e. at least a portion of the anode is consumed), the method involves exposing the oxidized portion of the anode to a chemical reductant such that the oxidized portion is reduced. In one embodiment, reducing this oxidized portion regenerates the anode to its initial state. In one embodiment, the anode is a metal  
20 which is oxidized to a metal oxide, and exposure of the metal oxide to a chemical reductant results in re-formation of the metal anode or to an oxidation state capable of oxidizing the fuel. In one embodiment, the chemical reductant is a fuel. This is advantageous in that the device does not require any new materials as the fuel available is capable of reducing the oxidized portion of the anode to the initial state of  
25 the anode.  
30



In one embodiment, the reduced portion, which results from reducing the oxidized portion, is capable of functioning as an anode again. "Functioning as an anode" involves either the operation of the anode as a battery or a fuel cell.

Another aspect of the invention provides a method for energy conversion, comprising the step of providing a device comprising a liquid metal anode. A portion of the anode is oxidized to form a metal oxide concurrent with the generation of electricity in the device. The anode can be oxidized by heating the device to any of the preferred operable temperatures disclosed herein when exposed to oxygen anions. Alternatively, the oxidized anode can be reduced by exposing the anode to a fuel, preferably at the temperatures disclosed herein.

The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not exemplify the full scope of the invention.

#### Example 1: An electrochemical device

A single electrochemical device, as exemplified by FIG. 2, is constructed as follows. Tubular electrolyte 15 is made of YSZ (yttria-stabilized zirconia,  $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ ) and has a thickness of 180  $\mu\text{m}$ . Tubular cathode 16 is made of LSM ( $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ ) and has a thickness of 300  $\mu\text{m}$ . A platinum wire functions as a cathode current collector (lead 18b), and a graphite rod functions as an anode current collector (lead 18a). The tube has a length of 3 cm, a diameter of 1 cm. The anode comprised either 8 g antimony; antimony alloy with 5% lead; indium; lead; antimony alloy with 10% tin; antimony alloy with 5% silver; antimony alloy with 50% indium; tin; or tin alloy with 5% Pb. The device is placed on a heating block with a temperature control.

#### Example 2: Propane Gas and Natural gas as fuel for recharging

To demonstrate that a device of the present invention can be operated without the addition of fuel, the device of Example 1 was heated and maintained at 960 °C. The device registered an open circuit voltage of 0.78V and a short current of 1.5 amp.

After operating for 30 min., there was no visible decrease in the power output. After a time from 2-8 h, the current dropped to zero and the open circuit voltage was 0.3 - 0.6 V.

Propane gas (Bernzomatic) or natural gas was introduced through an alpha-  
5 alumina tube (outside diameter 1.2 mm and inside 0.8 mm) into the liquid metallic anode. The end of the tube was submerged beneath the surface of the liquid at a gas flow rate of 50 mL/min.

After charging the device for 2 min. with propane gas, the short circuit current increased from zero to 0.3 amp and the open circuit voltage measured 0.79. After a 7  
10 minute charge, the device registered a current of 1.2 amp and a voltage of 0.76 V. Exhaust gas started to show some smoke or carbon soot. With an additional 2 min. charge, the current reached 1.5 amp and voltage 0.76 V. The amount of light smoke was another indication of the degree of charge. More charge did not change the current and voltage.

15 Delivery of propane gas was ceased and the device continued to run for a time greater than 1h until it was exhausted. The device was then recharged with propane gas as described in this Example. This cycle was repeated for three days without noticeable change of power output.

20 Example 3: Diesel, gasoline and alcohol (denatured) as fuel for recharging

The device of Example 1 was heated and maintained at 990 °C without the addition of fuel. After the cell was exhausted (current was zero and open circuit voltage was 0.3 -0.6V), 5 µL of gasoline was injected through a microsyringe into the liquid metallic anode. A total of 5 injections was made within 5 min at a rate of 5  
25 µL/min. Gray smoke was observed during each injection. After recharging with gasoline, the cell gave a current of 2.0 amp (from zero) and voltage of 0.75 V.

To demonstrate the ability of the device to operate with different fuels, the cell was then heated and maintained at 990 °C. After the cell was exhausted (current was zero and open circuit voltage was 0.3 -0.6V), 2 µL of denatured alcohol was injected  
30 through a microsyringe into the liquid anode. A total of 40 injections were made in

13 minutes at a rate of 6.2  $\mu\text{L}/\text{min}$ . Little smoke was observed during each injection. After recharging with alcohol, the cell gave a current of 0.3 to 0.5 amp and voltage of 0.72 V.

The cell was then heated and maintained at 990  $^{\circ}\text{C}$ . After the cell was  
5 exhausted (current was zero and open circuit voltage was 0.3 -0.6V), 4  $\mu\text{L}$  of diesel was injected through a microsyringe up to the surface of the liquid metallic anode. A total of 20 injections were made within 20 minutes at a rate of 4  $\mu\text{L}$  per minute. Heavy smoke was observed during each injection. After recharging with diesel, the cell gave a current of 0.3 to 0.5 amp and voltage of 0.72 V.

10

#### Example 4: Carbon black as fuel for recharging

This Example demonstrates the ability of the device of the present invention to operate with a solid fuel. The device of Example 1 was heated and maintained at 980  $^{\circ}\text{C}$ . After the cell was exhausted (current was zero and open circuit voltage was 0.3 -  
15 0.6V), carbon grains (size 0.3 - 0.6 cm) were added inside the cell. After recharging with 0.1 g of carbon, the cell gave a current of 0.3 to 0.5 amp and voltage of 0.72 V. After recharging with 0.1 g more carbon, the cell gave a current of 0.5 - 1.0 amp and voltage of 0.763. After recharging with 0.21 gram more carbon, the cell gave a current of 1.1 to 1.3 amp and voltage of 0.79 to 0.87 volt. After recharging with 0.17  
20 gram more carbon, the cell gave a current of 1.5 amp and 0.9 to 0.92 V.

#### Example 5: Weight analysis for multi-unit stack for liquid fuel

FIG. 5 shows exemplary dimensions of a stack of the present invention. Table 1 lists a weight for each component of the stack. Weights of liquid fuels such as  
25 gasoline, kerosene and diesel are based on a power density of 4  $\text{kW}/\text{m}^2$ . Fuel and tank are not included.

Table 1

Component	Dimension and size	Weight, lb
Ceramic electrolyte	25,000 x 0.01 cm <sup>3</sup> (250 cm <sup>3</sup> )	3.3
Ceramic cathode	25,000 x 0.015 cm <sup>3</sup> (375cm <sup>3</sup> )	5.0
Ceramic interconnect	3,500 cm <sup>3</sup> (1,500 cm <sup>3</sup> )	46
Liquid metallic anodic	3,750 cm <sup>3</sup> (2,500 cm <sup>3</sup> )	50
Air delivery system		2
Fuel delivery system		2
Insulation		3
Case & support		20
Total Weight		131

An example stack can comprise a 60-stack of planar electrochemical devices.

- 5 Each stack can have a size of 8 in. (203 cm) x 8 in. (203 cm) = 64 in.<sup>2</sup> (412 cm<sup>2</sup>), with a power output of 412 cm<sup>2</sup> x 0.4 watt/cm<sup>2</sup> = 165 watt each. Each stack can have a thickness of 0.4 cm (0.01 cm for the electrolyte, 0.02 cm for the cathode, 0.22 cm for the interconnect and 0.15

cm for the liquid metallic anodic component). In this example, the total stack length is  $60 \times 0.4 \text{ cm} = 24 \text{ cm}$  (9.5").

The liquid fuel cell is rated at 10 kW (165 watt/stack x 60 stacks) with the stack size of 8 in. (203 cm) x 8 in. (203 cm) x 9.5 in. (24 cm).

- 5 Including insulation (1.5" thickness), case & support, air and exhaustive flow conduits, and a preheating, the stack can have a volume of one cubic foot and a weight of 131 lb. This does not include the fuel and a fuel tank.

Example 6: Weight analysis for multi-unit stack for solid fuel

- 10 FIG. 6 shows exemplary dimensions of a stack of the present invention for a solid fuel such as carbon. The carbon can be placed inside as part of the device or can be charged from the outside periodically. Table 2 lists a weight for each component of the stack. 46 lb of carbon can be stored inside the device. Of course, the amount of carbon stored inside could be more or less, depending on the mission.

15

Table 2

Component	Dimension and size	Weight, lb
Ceramic electrolyte	$25,000 \times 0.01 \text{ cm}^3$ (250 cm <sup>3</sup> )	3.3
Ceramic cathode	$25,000 \times 0.015 \text{ cm}^3$ (375cm <sup>3</sup> )	5.0
Ceramic interconnect	$3,500 \text{ cm}^3$ (1,500 cm <sup>3</sup> )	46
Liquid metallic anodic	$3,750 \text{ cm}^3$ (2,500 cm <sup>3</sup> )	50
Air delivery system		2
Carbon plate as fuel	0.3 cm x 25 cm x 20 cm x 60	46
Carbon & liquid guide		5
Insulation		5
Case & support		25
Total Weight		<b>187 lb</b>

- 20 An example stack can comprise a 60-stack of planar fuel cell stacks. In this example, each stack has a surface area of 8 in. (203 cm) x 8 in. (203 cm) = 64 in.<sup>2</sup> (412 cm<sup>2</sup>), with a projected power output of  $412 \text{ cm}^2 \times 0.4 \text{ watt/cm}^2 = 165 \text{ watt}$  each. A gap of 0.6 cm between each stack may be longer than that of the liquid fuels (cf. 0.4 cm). Exemplary dimensions: electrolyte = 0.01 cm; cathode = 0.02 cm; interconnect = 0.22 cm; and carbon and liquid anode = 0.35 cm. In this example, a total stack
- 25 length is  $60 \times 0.6 \text{ cm} = 36 \text{ cm}$  (14").

An additional guide (5 lb) extending out of the stack can be provided for guiding carbon plate and storing excess liquid metals.

The carbon cell is rated at 10 kW (165 watt/stack x 60 stacks) and has a dimension of 15" x 16" x 12" and weighs 187 lb with 46 lb of carbon stored inside as  
5 fuel.

With the 46 lb carbon fuel and at 40% fuel efficiency, the unit will produce 73 kW-hours, equivalent to 860 watt-hours/kilogram.

Increasing carbon fuel load, will improve the energy density. The theoretical limit for carbon is 3,520 watt-hours/kilogram at 40% fuel efficiency.

10

Example 7: Analysis of device components after operation

After operating the device of Example 1 as described in Example 2, the device was smashed to allow observation of the internal components. In the interface between the anode and the electrolyte, a yellow powder or white powder was  
15 observed. Without wishing to be bound by any theory, it is proposed that this yellow or white powder comprises consumed anode, i.e., a metal oxide such as antimony oxide or a mixed antimony/lead, antimony/tin, antimony/silver, tin and antimony/indium oxide. Interestingly, in the anode/electrolyte interface immediately adjacent the fuel source, no powder was observed. It is believed that the absence of  
20 powder in this portion of the cell provides evidence that the fuel is capable of reducing any metal oxide back to the metal.

**Improvements to Chemically Rechargeable Anode Electrochemical Systems**

In another embodiment, the present invention is directed to an electrochemical  
25 system including an electrochemical device of any of the types described herein and a control system connected to the electrochemical device.

Referring now to FIG. 10, in one embodiment, the present invention includes an electrochemical system 300 including an electrochemical device 32 including an anode 34 constructed of a material such that anode 34 is chemically rechargeable.  
30 Electrochemical device 32 may be any device capable of electrochemical operation so long as it comprises an anode 34 that is chemically rechargeable. For example,



electrochemical device 32 may operate as a fuel cell or battery. In an alternate embodiment, electrochemical device 32 may be any device capable of electrochemical operation so long as the anode comprises a liquid. While any of the embodiments of electrochemical devices disclosed above, as well as conventional electrochemical devices, may be suitable for use with electrochemical system 300 in particular embodiments, embodiments of electrochemical devices including chemically rechargeable liquid metal anodes are particularly preferred.

Electrochemical system 300 may include a control system 303. Control system 303 may be any system capable of monitoring one or more properties of electrochemical system 300, such as one or more properties of electrochemical device 32, and controlling one or more properties of electrochemical system 300 based upon this monitoring. Examples of properties of electrochemical device 32 that may be monitored and/or controlled include fuel feed rate, temperature profile of the fuel feed system, anode oxide concentration, fuel concentration in the anode, operating temperature, contaminant concentration, anode level, fuel composition, fuel heating value, temperature profile of the electrochemical device, air or oxygen feed rate to the cathode; oxygen concentration in the cathode feed or exhaust, exhaust composition, concentration of particular species in the exhaust, voltage, current, resistance, AC impedance profile, power output, fuel efficiency, fuel utilization, and the like. Examples of possible exhaust species that may be monitored and/or controlled include carbon monoxide, hydrogen, carbon dioxide, sulfur oxides, nitrogen oxides, volatile organic compounds, hydrogen sulfide, and combinations thereof.

Control system 303 may operate by any mechanism that provides the desired control of electrochemical system 300. For example, control system 303 may include at least one controller 310. Controller 310 may include, for example, digital, analog, or digital and analog systems. Preferably control is centralized in a single controller 310, which may be simple, reliable and inexpensive. It should be understood, however, that control system 303 may include multiple controllers 310, for example controlling different properties of electrochemical system 300, and may include controller/subcontroller combinations. Other controllers and related systems are

known in the art, for example in PCT/US00/29652, which is hereby incorporated by reference herein in its entirety.

Where control system 303 includes at least one controller 310, such controller 310 may, for example, receive input signals, modify and/or interpret these signals and provide output signals. Input signals may come from any part of electrochemical system 300 where it is desired to measure a property. Similarly, output signals may be sent to any part of electrochemical system 300 where it is desired to control a property. In some instances, a property or group of properties may be monitored or controlled indirectly by monitoring or controlling a related property or group of properties, as will be discussed in greater detail below.

Input signals and output signals to and from controller 310 may be any type of signal and may be sent via any appropriate medium. For example, input and output signals may be pneumatic signals carried by tubing, analog electrical signals carried by conductive wires, digital electrical signals carried by conductive wires or optical signals carried by fiber optic cables. Combinations of signal types and other signal types are also possible. In some cases, signals may share transfer media. For example, a pump may provide both input and output signals via a single connection 305, such as an electrical cable.

One property of electrochemical system 300 that may be monitored and/or controlled is the concentration of one or more constituents within anode 34, also referred to herein as anode species. For example, the presence of excess fuel or, conversely, excess oxidation of anode 34 may be monitored and/or controlled. Monitoring anode oxide concentration may provide information regarding whether electrochemical device 32 is operating primarily as a fuel cell or primarily as a battery and may allow this operation to be adjusted where desired. For example, where it is desired to operate electrochemical device 32 as a fuel cell, when anode oxide concentrations above a certain level are detected, a property of the system may be modified to reduce this level and emphasize fuel cell operation. Similarly, monitoring the concentration of fuel 41 in the anode may provide a warning that electrochemical device 32 is experiencing a build up of fuel 41, or a component or components thereof, such as elemental carbon, which may adversely effect the operation of

electrochemical device 32, such as by clogging of areas 42 through which exhaust may otherwise escape. Another property of electrochemical device 32 that may be monitored or controlled is the level of oxygen in the cathode exhaust, for example to ensure that sufficient oxygen is provided to the cathode.

5           Concentration of constituents in the anode is an example of a property that may be measured indirectly, however, it should be understood that this is a matter of convenience, rather than necessity. For example, rather than measuring the amount of fuel or oxidized anode directly within the anode, this concentration may be  
10           determined based upon the concentration of fuel that is incompletely oxidized in the exhaust from electrochemical device 32. In one embodiment, the concentration of CO in the exhaust from electrochemical device 32 is monitored and correlated to the anode oxide concentration and/or fuel concentration in the anode. As an alternate example, the concentration of anode oxide or fuel in the anode may be determined based on either or some combination of the AC impedance profile, the current, the  
15           resistance, the power output, the fuel efficiency, the fuel utilization, and the voltage produced by electrochemical device 32. As further examples, the concentration of anode oxide or fuel in the anode may be determined based on the concentration of water, hydrogen or other gas in the exhaust, the pressure of the exhaust, and the like. It should now be appreciated that any property may be measured indirectly if it is able  
20           to be correlated to another property that may be measured. It should also be appreciated that more than one property or a combination of properties may correlate to a property that is desired to be measured indirectly and that any of these properties, or more than one of them, may be selected to measure. The correlation between two properties, such as CO in the exhaust to fuel concentration in the anode, may vary for  
25           the particular properties and electrochemical device and may be determined empirically or theoretically as appropriate. For example, as the CO level increases the carbon level in the anode may be inferred to be higher or, conversely, the anode oxide level lower.

          Another example of a property that may be measured indirectly is oxygen use  
30           by the cathode. For example, oxygen use may be measured based on the concentration of oxygen in the cathode exhaust. Alternatively, it could be measured

based upon a property of the anode, such as any of the properties mentioned above, such as exhaust species concentration, AC impedance profile, resistance, power output, fuel efficiency, fuel utilization, current, voltage, and combinations thereof.

Properties may be monitored by any device or system capable of providing the  
5 desired information. For example, properties may be monitored by conventional sensors for the given property, such as thermocouples for temperature, pressure transducers for pressure, gas chromatographs for gas composition, manometers for pressure, gas specific sensors for particular gasses, and the like, or the electrical output of the device itself. Such sensors may be placed as close to the point where it  
10 is desired to know the property to be measured as practical. Sensors may be in placed in communication with control system 303, for example by being connected to a controller 310 with a connection 305, as described above. If controller 310 is, or includes, a digital controller, analog signals from sensors may be converted to digital signals with use of analog to digital converters. Similarly, signals sent from a digital  
15 controller to analog control devices may be converted to analog signals by a digital to analog controller. Analog controllers sending and/or receiving signals from digital devices may also use converters.

Properties may be controlled by any device or system capable of effecting a desired change in a property. For example, properties may be controlled with  
20 conventional property modifying devices, such as heat exchangers and heaters for temperature, valves and pumps for pressure and flow rate, and the like. Such devices may be placed as close to the point where it is desired to control the property as practical. Property modifying devices may be in placed in communication with control system 303, for example by being connected to a controller 310 with a  
25 connection 305, as described above.

As with monitoring of properties, control of properties may be exercised indirectly. For example, concentration of species in anode 34 may be controlled by controlling what is fed to anode 34, such as fuel 41, or what is fed to cathode 6, such as oxygen-containing gas. In one embodiment, when the concentration of anode  
30 oxide is determined to exceed a certain level, the amount of fuel provided to the anode may be increased to reduce the anode oxide back to anode. In another embodiment,

where the concentration of fuel in the anode is determined to exceed a certain level, the amount of fuel provided to the anode may be decreased so that the excess fuel in the anode compartment may be consumed. As an alternate example, the temperature of electrochemical device 32 may be controlled by controlling a flow of air or other oxygen containing gas to the cathode. If the temperature rises to undesirable levels, the air flow may be increased to levels beyond that required for stoichiometric completion of the reaction. The heat capacity of the unreacted air may thus be used to carry excess heat out of the system. Conversely, the system temperature may be increased by decreasing the airflow. However, the airflow will typically not be decreased to a point at which the system is chemically starved for oxygen. Where it is not desired to decrease the air flow, heat may be added to the system to maintain the system at a desired operating temperature. However, such added heat is a parasitic energy load on the system and therefore reduces overall efficiency.

Referring now also to FIG. 11, where it is desired to regulate fuel flow to the anode, a fuel delivery system 301 may be used. Fuel delivery system 301 may be constructed in any manner and with any material(s) that allow fuel flow to the anode to be controlled as desired. Where fuel delivery system 301 is used it may be constructed for long, reliable use, such as by being simple and accurate. For example, fuel delivery system 301 may include structure to cause fuel to flow into the anode and structure to control this flow. In some embodiments, flow may be provided by a pump appropriate to the fuel type. In cases where pressurized gas is used as a fuel, the pressure in a gas reservoir 314 may supply the required pressure for flow of the fuel into electrochemical device 32. In other cases, such as where the fuel is solid, it may be possible to supply the fuel using a conveyor system, screw feed or other apparatus or system for the transport of solids. Solid fuels may also be gasified and supplied accordingly. Flow control may be provided by a mass flow controller, valve 316, restriction, critical orifice, combination of these devices, or the like. Alternatively, variably providing the pressure needed to instigate flow, such as by turning on and off a pump, or opening and closing a valve to a pressurized reservoir may be used to accomplish both flow generation and flow control.



In one embodiment where the fuel is a gas or supercritical fluid, fuel delivery system 301 uses one or more restrictions of known flow properties and a simple on/off valve to provide fuel to anode 34. Typically, such a restriction will be an orifice, but it may also comprise a frit, filter, or the like. The restriction may be operated as a critical restriction, meaning that the pressure difference across the restriction may be maintained at a level such that the flow through the restriction is dependent only on the upstream pressure and the geometry of the restriction. Flow through a restriction dependant only on upstream pressure is referred to herein as “critical flow.” It should be appreciated that, even where true critical flow is not achieved, substantial pressure drops across a restriction may create a condition where the flow rate through the restriction is only weakly dependent on downstream pressure. This weakened dependence on downstream pressure may lead to sufficient predictability of flow rate for some embodiments. For example, an upstream to downstream pressure ratio of 1.1:1 across the restriction may be enough for some embodiments, while a upstream to downstream pressure of 1.25:1 or even 2:1 or more may be preferred for others. Where critical or near-critical flow conditions and consistent pressure upstream of the restriction are maintained, simple, accurate on/off feed to anode 34 may be provided. Varied flow rates may be achieved by pulsing the flow through the restriction to provide the desired overall flow rate.

In another embodiment using a restriction, the pressure upstream of the restriction may be varied to vary the flow through the restriction. For example, a controller associated with the control system may be connected to a pressure sensor, such as a pressure transducer, upstream of the restriction to verify that the upstream pressure is sufficient to produce the desired flow and to control this pressure with a pump, valve, or other device or system, where it is desired to control the flow rate in this manner. In embodiments including multiple electrochemical devices, several restrictions, or sets of restrictions, may be incorporated into a manifold system to supply fuel to the electrochemical devices from a single source of pressurized fuel. The use of critical, or near-critical flow may allow consistent flow to all of the electrochemical devices despite varying pressures within the electrochemical devices.



It should be understood that where a liquid anode is used, care may be taken to ensure that the fuel is not injected into the anode in a manner resulting in the splashing of the liquid anode outside its intended confines. Such splashing may result in both equipment damage and a safety hazard. In some embodiments, a structure  
5 may introduced to reduce the danger of splashing, such as a splatter guard or a chimney. Such a structure may be constructed of a material that is resistant to high temperatures, such as  $\alpha$  alumina or zirconia.

Fuel delivery system 301 may be constructed to improve the flow of fuel to anode 34. For example, fuel delivery system 301 may be constructed to reduce  
10 clogging. In some embodiments, clogging may occur in a fuel delivery system from breakdown of fuel into multiple components, one of which is solid carbon as the fuel enters a high temperature zone prior to entering anode 34. For example, one mechanism of breakdown for propane fuel is shown in eq. (5):



Many fuels break into a variety of components including carbon. Furthermore, many fuels are broken down through more than one mechanism. In any mechanism where solid carbon is formed, the carbon can deposit and build up within electrochemical  
20 system 300, such as within fuel delivery system 301. This deposition of carbon is known as coking. Clogging may also occur where the anode is a liquid metal and is allowed to flow into a portion of fuel delivery system 301 that is cool enough that the anode may solidify therein.

Where clogging due to breakdown of fuel is a concern, an anti-coking agent  
25 318 may be used. By anti-coking agent, it is meant any material(s) that results in reduced solid carbon build-up. Preferably, anti-coking agent 318 inhibits the breakdown of fuel through mechanisms resulting in carbon formation or promotes formation of fuel from solid carbon, such as by gasification through shift reactions. Anti-coking agent 318 may simply replace a material that would typically be present  
30 and is known or suspected to promote the breakdown of the fuel with a material that is known or suspected to promote the breakdown of fuel to a lesser extent. Anti-coking

agent 318 may work by any mechanism that provides the desired anti-coking function. For example, anti-coking agent 318 may be added to the fuel itself.

In some embodiments, anti-coking agents may include products of a reaction that may lead to fuel breakdown, such as a cracking or carbon shift reaction, and may  
5 drive the equilibrium of the reaction away from breakdown of the fuel. Alternatively, such anti-coking agents may be viewed as providing needed materials to allow such reactions to proceed in the opposite direction, i.e. from solid carbon to more complex fuel. It is not important whether the anti-cracking agent promotes a desired reaction or inhibits an undesired reaction and the reactions given herein are provided by way  
10 of example and should not be interpreted as limiting the scope of the invention to any particular theory. For example, carbon monoxide and hydrogen fuels may react to form carbon and water as illustrated in eq. (6).



15

Adding water to the fuel increases its concentration, driving the equilibrium away its formation and away from the formation of solid carbon. Similarly, carbon monoxide fuel may react to form carbon and carbon dioxide as illustrated in eq. (7).

20



As with water above, adding carbon dioxide to the fuel will increase its concentration, driving the equilibrium away from its formation and away from the formation of solid carbon. Oxygen may also be added as it may form carbon dioxide and act as an anti-  
25 coking agent.

It should be understood that anti-coking agents intended to shift the equilibrium of a reaction resulting in the breakdown of fuel need not necessarily be added in stoichiometric amounts. For example, the amount of anti-coking agent required to sufficiently inhibit a reaction may be more or less than that required to  
30 complete it or to achieve static equilibrium conditions. In some embodiments, it is preferred to add as little anti-coking agent to the fuel as possible because anti-coking

agents may reduce the efficiency of the electrochemical device. For example, adding gas to an electrochemical device in the form of an anti-coking agent may reduce the contact between the anode and the electrolyte due to occlusion of the electrolyte by bubbles of fuel and anti-coking agent. This may be particularly true where the anode is a liquid, such as a metal, and the electrolyte is a material, such as a ceramic, that is not wetted by the liquid. In these cases, the bubbles may eliminate electrical contact between the electrolyte and the anode, rendering the occluded area inactive while the bubble is present. As the amount of fuel, anti-coking agents, reaction products, and/or combinations thereof increases, the amount of area available for the production of electricity decreases, thereby lowering the power capability and efficiency of the electrochemical device. Furthermore, large amounts of anti-coking agents may scavenge heat from the electrochemical system due to their heat capacity. This is a particular problem in situations where the device is operated at relatively low power, because the heat provided by the electrochemical reactions may not be sufficient to overcome the heat losses of the system such as heat loss through the case and heat carried away from the system by excess reactants passing through the system. In such situations, heat may be added to the electrochemical system to prevent the system from cooling to undesirably low temperatures. As noted previously, this additional heat is a parasitic load and therefore reduces overall system efficiency. In situations where additional heating is required, care may be taken to minimize the mass flow rate of all species passing through the system, such as excess air, fuel and some anti-coking agents.

Where anti-coking agents 318 are added to fuel 41, they may be added in any manner that results in the desired anti-coking function while still resulting in effective fuel delivery. For example, anti-coking agents may be added directly to the fuel stream and may be mixed with the fuel. Mixing may be performed by any mixing device or system capable of providing a desired level of mixing, such as static mixers, active mixers and the like. Anti-coking agents may be introduced into the fuel from any source. For example, where the anti-coking agent is water, it may be added to the fuel stream by direct injection to water, or from a steam line or boiler. As an alternate example, gaseous fuel 41 may be bubbled through water in a bubbler 320 such that

the gas picks up water in vapor form. The amount of water picked up by the gas may be adjusted by warming or cooling the water with a heating device 324 such as a heat exchanger, electric heater, or the like, thereby increasing or decreasing the water's partial pressure in the fuel stream. Care may be taken to prevent the fuel gas carrying the water from reducing in temperature to the point that the water vapor condenses in fuel delivery system 301. Other liquid anti-coking agents may also be added in this manner. Where anti-coking agent 318 is gaseous, such as carbon dioxide and/or steam, it may be supplied from a reservoir external to fuel delivery system 301. Where anti-coking agent 318 is an exhaust gas, such as carbon dioxide and/or water, it may be supplied as a recycle from the exhaust from electrochemical device 32.

Anti-coking agent 318 may also be part of fuel delivery system 301. For example, anti-coking agent 318 may be connected to some portion of fuel delivery system 301. In one embodiment, the anti-coking agent is placed in fuel delivery system 301 where fuel breakdown may occur. For example, anti-coking agent 318 may be located in a hot zone 322 of fuel delivery system 301. By "hot zone," it is meant a region in which the temperature is high enough to cause substantial coking. Accordingly, the particular temperature that constitutes a hot zone may vary, for example, based upon the fuel and the nature of the fuel delivery system. For example, where the fuel delivery system is easily clogged or a long operation cycle is required, the temperature defining a hot zone may be lower as a lower amount of coking may be substantial. Typically, some portion of fuel delivery system 301 adjacent anode 34 will be a hot zone. For example, a feed conduit 40 leading into anode 34 may include a hot zone 322. Anti-coking agent 318 may be located within hot zone 322 in any manner that contacts the anti-coking agent to the fuel such that its function may be performed. For example, anti-coking agent 318 may be connected to the inside of fuel delivery system 301, such as on the inside of feed conduit 40. In one embodiment, feed conduit 40 is constructed of, or coated on the inside with, an anti-coking agent, such as a material known or suspected not to catalyze the breakdown of fuel, such as copper. In another embodiment, feed conduit 40 is constructed of, or coated on the inside with, an anti-coking agent known to promote the formation of fuel from solid carbon, such as copper, nickel, ruthenium, or cerium. Other anti-

coking agents may include alkaline or rare earth metals and may include, for example, rhodium, osmium, aluminum, calcium, magnesium, sodium, and potassium.

It should be appreciated that, while in some instances similar materials may be used, the use of anti-coking agents is distinct from the use of conventional fuel reformers. Specifically, anti-coking agents reduce the amount of coking in the cell, but do not break down all, substantially all, or even typically even 75% or 50% of the fuel into constituents, as with a conventional reformer. It should also be appreciated that the electrochemical devices disclosed herein may be used with conventional reformers. In some embodiments, the use of a conventional reformer may eliminate the need for anti-coking measures.

In another embodiment, anti-coking agent 318 is packed into a portion of fuel delivery system 301 such that the fuel passes over and/or through the anti-coking agent. In this embodiment, the anti-coking agent may be coated onto a support.

In another embodiment, breakdown of fuel prior to entry into the anode is inhibited by reducing or eliminating hot zones from fuel delivery system 301. Hot zones may be reduced or eliminated in any manner that allows fuel delivery system 301 to operate as desired. For example, hot zones may be reduced by thermally insulating fuel delivery system 301 from hot portions of electrochemical device 32. As an alternate example, a portion of electrochemical device 32 may be reduced in temperature such that a hot zone 322 will not be created in fuel delivery system 301 where it is near electrochemical device 32. In another embodiment, a portion of anode 34 is reduced in temperature, creating a cold zone. For example, where anode 34 comprises a liquid, a portion of it may be allowed to occupy a portion of fuel delivery system 301, such as feed conduit 40, where it may remain sufficiently cool that a hot zone is not created within fuel delivery system 301. As an alternative example, a portion of electrochemical device 32 adjacent to fuel delivery system 301 may be cooler than the remainder of electrochemical device 32, such that it does not create a hot zone 322. Where a portion of anode 34 is allowed to cool, it may remain sufficiently warm to remain in liquid state, such that fuel may still be easily introduced therein.

Several examples of anti-coking agents and systems have been described. It should be understood that these are not the only possible anti-coking agents or systems. It should further be appreciated that different anti-coking agents and systems may complement one another and that any combination of anti-coking agents  
5 may be used.

Fuel delivery system 301 may feed fuel 41 to any portion of the anode of electrochemical device 32. Preferably, fuel delivery system 301 delivers fuel 41 such that it facilitates efficiency of electrochemical device 32. For example, fuel 41 may be fed such that contact between fuel 41 and anode 34 is maximized and/or such that  
10 contact between anode 34 and an electrolyte 35 is maximized. Where anode 34 is a liquid anode, and fuel 41 has a lower density than anode 34, fuel 41 may be introduced into the bottom of electrochemical device 34 such that it passes upward through anode 34. For example, where fuel 41 is a gas, it may be bubbled upward into electrochemical device 32, improving its contact time with anode 34. Various  
15 configurations may be used to introduce a gaseous fuel to the bottom of anode 34. For example, in one embodiment, fuel 41 is bubbled up through the bottom of electrochemical device 32, while, in another embodiment, a feed tube extends into anode 34 from above and releases fuel 41 near the bottom of anode 34. The latter embodiment may suffer from the drawback that the feed conduit passing through  
20 anode 34 may constitute a hot zone and, further, bubbles of fuel may travel up the outside of the feed tube rather than along the electrolyte, as will be described in greater detail below.

Where fuel 41 is introduced into liquid anode 34 as bubbles of gas, the size, shape and position of the bubbles may affect the performance of electrochemical  
25 device 32. Generally, it is preferred that fuel 41 be present at electrolyte 35 so that the fuel may be oxidized directly, rather than anode 34 being oxidized and then reduced by the fuel. The presence of fuel 41 at electrolyte 35 also may inhibit or reduce formation of a layer of anode oxide at or on electrolyte 35 or may chemically reduce back to anode material a layer of oxidized anode material that may have  
30 already formed and been adhered to the electrolyte. Such a layer of oxidized anode might otherwise increase the resistance across electrochemical device 32, lowering its



efficiency and power output. Accordingly, it is preferred to introduce bubbles of fuel 41 into anode 34 such that they travel along the interface of electrolyte 35 and anode 34. Conversely, it is preferred not to introduce fuel bubbles such that they travel up another surface, such as a feed conduit or lead 38a. Fuel bubbles traveling along lead 38a are particularly undesirable, as they occlude lead 38a, reducing the surface area in contact with anode 34.

Control of bubble formation of fuel 41 may require special consideration where anode 34 is a liquid that does not wet the material that electrolyte 35 is constructed from, such as where anode 34 is a liquid metal and electrolyte 35 is a typical ceramic electrolyte material, such as yttria-stabilized zirconia (YSZ). Such conditions may increase bubble size, result in unusual bubble shapes, and encourage bubbles to stick to the unwetted surface. In one embodiment where anode 34 does not wet electrolyte 35, fuel 41 is introduced through feed conduit 40 at the bottom of anode 34. In this embodiment, fuel 41 is believed to form a bubble on the bottom of anode 34 that grows until it contacts a wall ascending from the bottom (typically formed by electrolyte 32), at which point it travels up the wall.

Where fuel 41 is fed from the bottom of anode 34 and anode 34 is a liquid anode, fuel 41 may be fed such that anode 34 does not enter some or all of fuel delivery system 301. For example, fuel delivery system 301 may include structure, such as an anode flow prevention device, that allows fuel to pass, but not anode 34, or allows material to pass in only one direction. In some embodiments, a one-way valve may be used as an anode flow prevention device to prevent the ingress of anode 34 into undesired portions of fuel delivery system 301. Such a valve may be biased to be normally closed and may be opened by pressure of fuel 41. In other embodiments, an anode flow prevention device may include structure, such as a membrane or orifice, through which fuel 41 can pass, but not anode 34. For example, the anode flow prevention device may include one or more orifices sized such that the surface tension of the anode 34 prevents the anode from passing through the orifice. In selecting the size of the orifice(s) the surface tension and pressure of anode 34 may be considered. Such an arrangement may be particularly suitable where anode 34 does not wet the material from which the flow-preventing structure is constructed. One such

arrangement that has been found to be effective includes pores no greater than 0.3 mm in diameter; another such arrangement includes pores no greater than 0.1 mm in diameter. Where the pressure of the anode is low, for example in horizontal, planar embodiments, pore sizes may be as large as 3 mm for particular materials. In some  
5 embodiments, rather than using a discrete orifice or orifices, a porous structure, such as porous ceramic material, may be used as an anode flow prevention device to prevent the anode from entering undesired portions of fuel delivery system 301.

Embodiments of the present invention may include an oxygen delivery system to supply oxygen to the cathode of an electrochemical device. An oxygen delivery  
10 system may comprise any structure allowing oxygen to be delivered to the cathode. It should be appreciated that oxygen delivery systems are not limited to the delivery of oxygen alone and any gas containing oxygen, such as air, may be delivered.

Because of its ability to use a wide variety of fuels, including gaseous, liquid and solid fuels, as described above, electrochemical device 32 has greater flexibility  
15 than conventional fuel cells that may require a reformer to react the fuel into a form usable by the fuel cell. Furthermore, as electrochemical device 32 may be insensitive to sulfur in the fuel, for example because it forms a liquid with the anode and this liquid is easily removed because it may float on top of the anode, electrochemical device 32 may also avoid the need for a desulfurizer as is required in some fuel cells.  
20 For example, electrochemical device 32 may be useable with fuels having more than 1 part per million sulfur, more than 10 parts per million sulfur, more than 100 parts per million sulfur, or even higher sulfur concentrations. Additionally, sulfur compounds may oxidize in the electrochemical device, converting sulfur into sulfur oxides. Because sulfur in fuels may interfere with conventional reformers, electrochemical  
25 devices according to the present invention requiring neither a reformer nor a fuel desulfurizer are particularly useful.

In some embodiments, electrochemical device 32 may not completely consume the fuel provided to it, resulting in useable fuel in the exhaust. Also, because of the heat in the anode, excess fuel fed thereto may be broken into simpler  
30 fuels, such as CO or H<sub>2</sub>. Furthermore, the fuel, reaction products and air are heated as they pass through the electrochemical device. Thus, the total exhaust stream,

including the anode and cathode exhaust streams may contain a substantial amount of thermal energy in addition to the chemical energy of unused fuel from the anode exhaust stream. Where the electrochemical device is operated at pressures above ambient pressure, the exhaust from the cathode and/or anode may contain additional potential energy in the form of pressure.

Where desired, the energy contained within the anode and/or cathode exhaust may be captured in any way that increases the overall efficiency of the electrochemical system. For example, if the electrochemical system is operated at pressures exceeding ambient pressure, the exhaust stream may be fed to a system that recovers power from the exhaust through decompression, such as a system including a turbine. Alternatively, fuel in the exhaust may be burnt or fed to another electrochemical device to recover the energy therein. Fuel fed to a burner may be used for heating or burnt in an internal combustion engine, such as an engine using a turbine or piston and cylinder arrangement. Feeding the exhaust to an electrochemical device may be particularly desirable where the fuel has been broken into a simpler fuel, such as  $H_2$  or  $CO$ , which may be fed to an electrochemical device, such as a conventional solid oxide or molten carbonate fuel cell, that can only use such fuels. Where it is desired to recapture the fuel value of the fuel in the anode exhaust, such exhaust may be segregated from the cathode exhaust which may not have a substantial fuel value and may promote the breakdown of the fuel from the anode exhaust. Thermal energy may also be recaptured from the electrochemical system. Such energy may be used to expand a gas to generate mechanical or electrical energy, or it may be used for heating, for example through use of a heat exchanger. In one embodiment, thermal energy is used to provide heat or hot water to a building, making the electrochemical system a combined source of electrical and thermal energy for a business, dwelling, factory or the like. Heat may also be exchanged with inputs to the electrochemical device. For example, materials fed to the anode and cathode, such as fuel and oxygen may be preheated by exchanging heat with exhaust from the electrochemical device, or another electrochemical device. Heat may also be to power cooling in some instances.

Where it is desired to provide a fully reacted exhaust from the electrochemical device, for example to reduce pollution, the cathode and anode exhausts may be combined to react any remaining unburned fuel in the anode exhaust with any excess oxygen in the cathode exhaust. In an alternate embodiment, anode and cathode exhausts may be segregated.

Carbon dioxide may be removed from the exhaust of an electrochemical system according to the present invention, for example using a carbon dioxide separation system. A carbon dioxide separation system may be any system capable of removing a desired amount of carbon dioxide from an exhaust. It may be easier to remove carbon dioxide from a segregated anode exhaust. For example, in the carbon separation system, water may be condensed from the anode exhaust and carbon dioxide collected. This carbon dioxide may be prevented from escaping to the environment, reducing greenhouse gas emissions.

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that actual parameters will depend upon the specific application for which the methods and apparatus of the present invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described. Specifically, those of ordinary skill in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalent are intended to be encompassed by the following claims.

In the claims, all transitional phrases such as “comprising”, “including”, “carrying”, “having”, “containing”, “involving”, and the like are to be understood to be open-ended, i.e. to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of”, respectively, shall be closed or semi-closed transitional phrases as set forth in the United States Patent Office Manual of Patent Examining Procedures, section 2111.03.

What is claimed:

**Claims**

1. A method, comprising:  
measuring a property of an electrochemical system;  
correlating the measured property to a concentration of an anode species in an  
5 anode of an electrochemical device associated with the electrochemical system; and  
controlling the introduction of at least one of a fuel and oxygen to the  
electrochemical device based at least in part upon the concentration of the anode  
species in the anode of the electrochemical device.
- 10 2. The method of claim 1, wherein the measured property is selected from the  
group consisting of a concentration of an indicator species in an exhaust from the  
electrochemical device, a current generated by the electrochemical device, a voltage  
of the electrochemical device, an AC impedance profile of the electrochemical device,  
a resistance of the electrochemical device, a power output of the electrochemical  
15 device, a fuel efficiency of the electrochemical device, a fuel utilization of the  
electrochemical device, and combinations thereof.
3. The method of claim 1, wherein measuring a property of an electrochemical  
system comprises measuring a property of an exhaust from the electrochemical device  
20
4. The method of claim 3, wherein measuring a property of the exhaust  
comprises measuring the concentration of at least one species in the exhaust.
5. The method of claim 4, wherein measuring a property of the exhaust  
25 comprises measuring a property of an anode exhaust and wherein the at least one  
species is selected from the group consisting of carbon monoxide, hydrogen, carbon  
dioxide, sulfur oxides, nitrogen oxides, volatile organic compounds, hydrogen sulfide,  
and combinations thereof.

6. The method of claim 4, wherein measuring a property of the exhaust comprises measuring a property of a cathode exhaust and wherein the at least one species is oxygen.
- 5 7. The method of claim 3, wherein measuring a property of the exhaust comprises measuring the temperature of the exhaust.
8. The method of claim 1, further comprising:  
flowing a fuel into a bottom portion of an anode compartment of the  
10 electrochemical device, the anode compartment having the bottom portion and a wall ascending from the bottom portion;  
forming a bubble of the fuel on the bottom portion of the anode compartment until the bubble contacts the wall of the anode compartment; and  
allowing the bubble to travel up the wall of the anode compartment.
- 15 9. The method of claim 1, further comprising:  
flowing the fuel into the electrochemical device through a restriction sized and adapted to provide an upstream to downstream pressure ratio across the restriction of at least 1.1:1.
- 20 10. The method of claim 9, wherein the upstream to downstream pressure ratio across the restriction is at least 1.25:1.
11. The method of claim 10, further comprising flowing the fuel into the  
25 electrochemical device through a restriction comprising an orifice under critical flow conditions.
12. The method of claim 9, further comprising:  
supplying the fuel to a common reservoir; and  
30 flowing the fuel through a plurality of restrictions each associated with at least one of a plurality of electrochemical devices.



13. The method of claim 12, further comprising:  
varying a flow rate of fuel through the plurality of restrictions by varying the  
pressure in the common reservoir.
- 5
14. The method claim 1, wherein the anode is a liquid anode.
15. The method of claim 1, wherein the anode is a chemically rechargeable anode.
- 10 16. An electrochemical system, comprising:  
an electrochemical device comprising an anode, a cathode, and an electrolyte,  
the electrochemical device connectable to a fuel delivery system constructed and  
arranged to provide fuel to the electrochemical device, and connectable to an oxygen  
delivery system constructed and arranged to provide oxygen to the electrochemical  
15 device; and  
a control system, comprising:  
a sensor constructed and arranged to measure a property of the  
electrochemical device and produce a sensor signal representing the property,  
and  
20 a controller constructed and arranged to receive the sensor signal from  
the sensor, correlate the sensor signal to a concentration of an anode species in  
the anode, and provide a control signal to at least one of the fuel delivery  
system and the oxygen delivery system based, at least in part, on the  
concentration of the anode species in the anode.
- 25
17. The electrochemical system of claim 16, wherein the property is selected from  
the group consisting of a concentration of an indicator species in an exhaust from the  
electrochemical device, a current generated by the electrochemical device, a voltage  
of the electrochemical device, an AC impedance profile of the electrochemical device,  
30 a resistance of the electrochemical device, a power output of the electrochemical

device, a fuel efficiency of the electrochemical device, a fuel utilization of the electrochemical device, and combinations thereof.

18. The electrochemical system of claim 16, wherein the sensor is constructed and  
5 arranged to measure a property of an exhaust from the electrochemical device.

19. The electrochemical system of claim 18, wherein the property of the exhaust comprises the concentration of at least one species in the exhaust.

10 20. The electrochemical system of claim 19, wherein the exhaust comprises an anode exhaust and the at least one species is selected from the group consisting of carbon monoxide, hydrogen, carbon dioxide, sulfur oxides, nitrogen oxides, volatile organic compounds, hydrogen sulfide, and combinations thereof.

15 21. The electrochemical system of claim 19, wherein the exhaust comprises a cathode exhaust and the at least one species is oxygen.

22. The electrochemical system of claim 18, wherein the property is the  
temperature of the exhaust.

20

23. The electrochemical system of claim 16, wherein the sensor is constructed and arranged to measure a property that is at least one of an open circuit voltage, a current, an AC impedance, a power output and a resistance of the electrochemical device

25 24. The electrochemical system of claim 16, wherein the electrochemical device comprises an anode compartment constructed and arranged to at least partially contain a liquid anode, the fuel delivery system comprises a feed conduit fluidly connected to the anode compartment, and the electrochemical system further comprises an anode flow prevention device associated with the feed conduit.

30

25. The electrochemical system of claim 24, further comprising a liquid anode positioned at least partially within the anode compartment.
26. The electrochemical system of claim 24, wherein the anode flow prevention  
5 device is positioned at the end of the feed conduit.
27. The electrochemical system of claim 24, wherein the anode flow prevention device is porous.
- 10 28. The electrochemical system of claim 27, wherein a largest pore in the anode flow prevention device is less than 3 millimeters.
29. The electrochemical device of claim 27, wherein an average pore diameter of the anode prevention device is less than about 0.3 millimeter.
- 15 30. The electrochemical device of claim 29, wherein a largest pore diameter of the anode prevention device is less than about 0.3 millimeter.
31. The electrochemical system of claim 27, wherein pores in the anode  
20 prevention device are sized and shaped such that the surface tension of the anode prevents the anode from entering the pores.
32. The electrochemical system of claim 24, wherein the feed conduit is fluidly connected to a bottom of portion of the anode compartment.
- 25 33. The electrochemical system of claim 24, wherein the feed conduit is fluidly connected to a top portion of the anode compartment.
34. The electrochemical system of claim 33, wherein the feed conduit extends into  
30 the top portion of the anode compartment toward a bottom portion of the anode compartment.

35. The electrochemical system of claim 24, wherein the feed conduit is fluidly connected to a side portion of the anode compartment.
- 5 36. The electrochemical system of claim 16, further comprising:  
a fuel other than hydrogen, carbon monoxide, methane or a mixture thereof deliverable to the anode;  
wherein the electrochemical system is free of a fuel reformer.
- 10 37. The electrochemical system of claim 36, wherein the fuel is selected from the group consisting of solids, liquids, and combinations thereof.
38. The electrochemical system of claim 16, further comprising:  
a fuel including sulfur;  
15 wherein the electrochemical system is free of a fuel desulfurizer.
39. The electrochemical system of claim 38, wherein the fuel comprises more than 10 parts per million sulfur.
- 20 40. The electrochemical system of claim 39, wherein the fuel comprises more than 100 parts per million sulfur.
41. The electrochemical system of claim 16, further comprising:  
an exhaust conduit fluidly connected to the electrochemical device; and  
25 a second electrochemical device comprising a fuel delivery system in fluid communication with the exhaust conduit.
42. The electrochemical system of claim 41, wherein the second electrochemical device is selected from the group consisting of a solid oxide fuel cell, a fuel cell comprising a chemically rechargeable anode, a fuel cell comprising a liquid anode, a  
30 molten carbonate fuel cell, and combinations thereof.

43. The electrochemical system of claim 16, further comprising:  
an anti-coking agent selected from the group consisting of water, oxygen,  
carbon monoxide, carbon dioxide, and combinations thereof, deliverable to the fuel  
5 delivery system.
44. The electrochemical system of claim 43, wherein the anti-coking agent  
comprises an exhaust from the electrochemical device.
- 10 45. The electrochemical system of claim 43, further comprising a conduit fluidly  
connecting the exhaust to the fuel delivery system.
46. The electrochemical system of claim 16, further comprising:  
an anti-coking agent comprising a material selected from the group consisting  
15 of copper, nickel, platinum, oxygen, ruthenium, cerium, rhodium, osmium, aluminum,  
calcium, magnesium, sodium, other alkaline metals, other rare earth metals, and  
mixtures thereof, the anti-coking agent associated with at least a portion of a feed  
conduit of the fuel delivery system.
- 20 47. The electrochemical system of claim 16, wherein the anode is a liquid anode.
48. The electrochemical system of claim 47, wherein the anode comprises a cold  
zone associated with the fuel delivery system.
- 25 49. The electrochemical system of claim 48, wherein the cold zone comprises a  
portion of a feed conduit from the fuel delivery system, the portion of the feed conduit  
being occupied by a portion of the anode.
50. The electrochemical system of claim 16, wherein the anode is a chemically  
30 rechargeable anode.

51. The electrochemical system of claim 16, further comprising:  
an exhaust system; and  
a heat exchanger connected to the exhaust system.
- 5 52. The electrochemical system of claim 51, wherein the heat exchanger is  
constructed and arranged to be connectable to a building heating system.
53. The electrochemical system of claim 52, further comprising:  
a building heating system connected to the heat exchanger.
- 10 54. The electrochemical system of claim 51, wherein the heat exchanger is  
constructed and arranged to be connectable to a hot water supply system.
55. The electrochemical system of claim 54, further comprising:  
15 a hot water supply system connected to the heat exchanger.
56. The electrochemical system of claim 16, further comprising:  
an exhaust system; and  
a combustion system connected to the exhaust system.
- 20 57. The electrochemical system of claim 56, wherein the exhaust system  
comprises a cathode exhaust and an anode exhaust and only the anode exhaust is  
connected to the combustion system.
- 25 58. The electrochemical system of claim 56, wherein the combustion system  
comprises an internal combustion engine.
59. The electrochemical system of claim 56, wherein the combustion system  
comprises a heat exchanger.
- 30



60. The electrochemical system of claim 71, further comprising an exhaust system connected to a turbine.
61. The electrochemical system of claim 16, further comprising:  
5 an anode exhaust system; and  
a carbon dioxide separation system connected to the anode exhaust system.

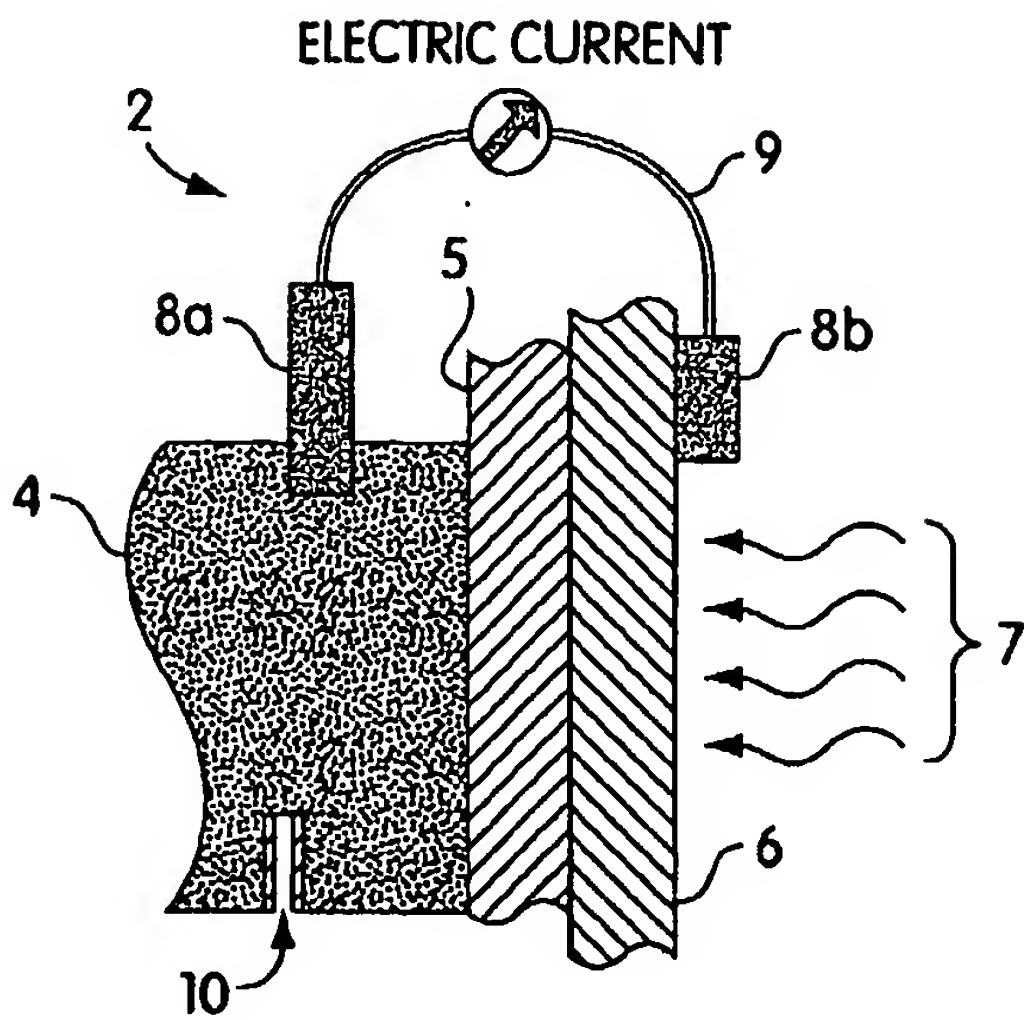


Fig. 1

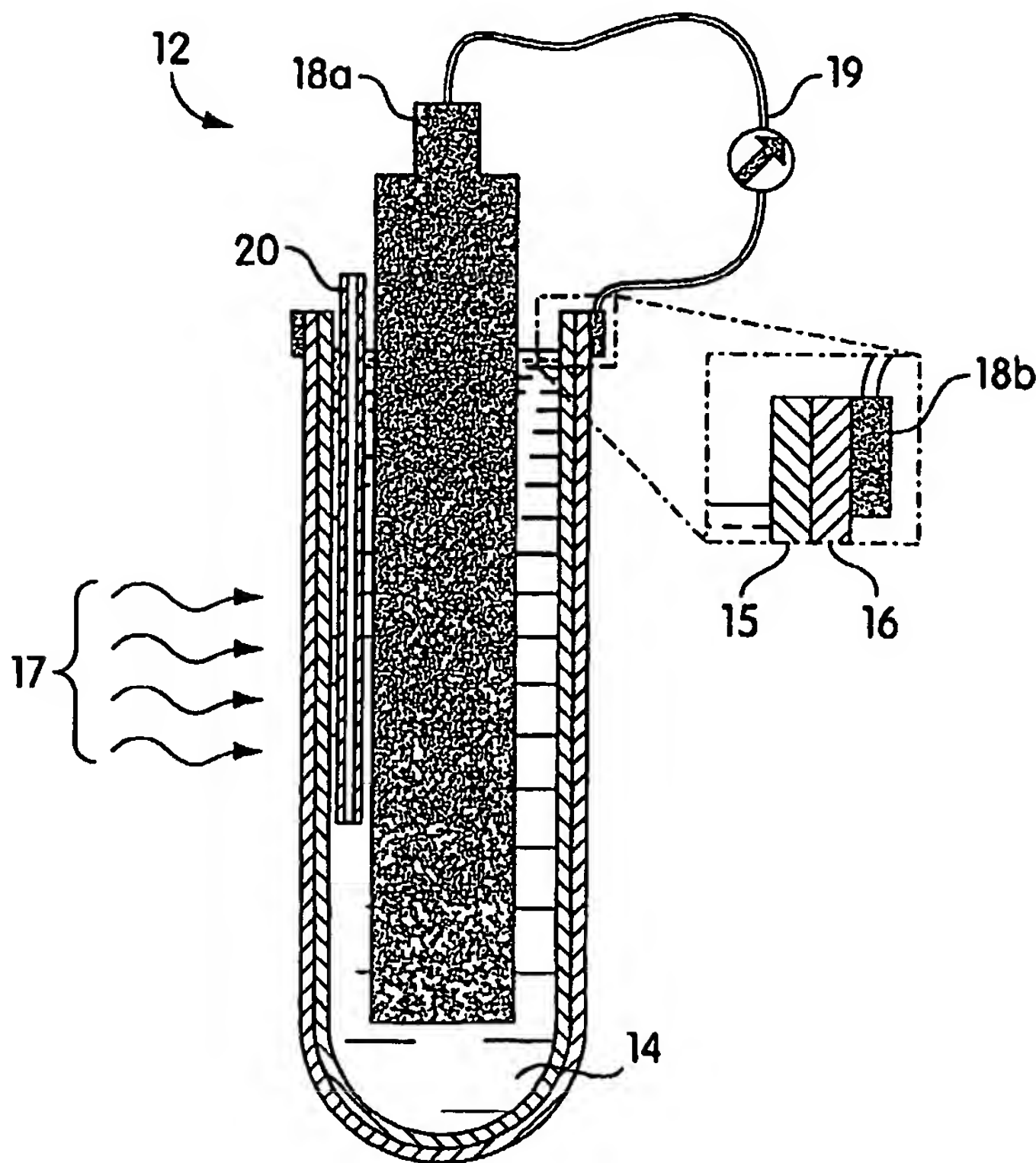


Fig. 2

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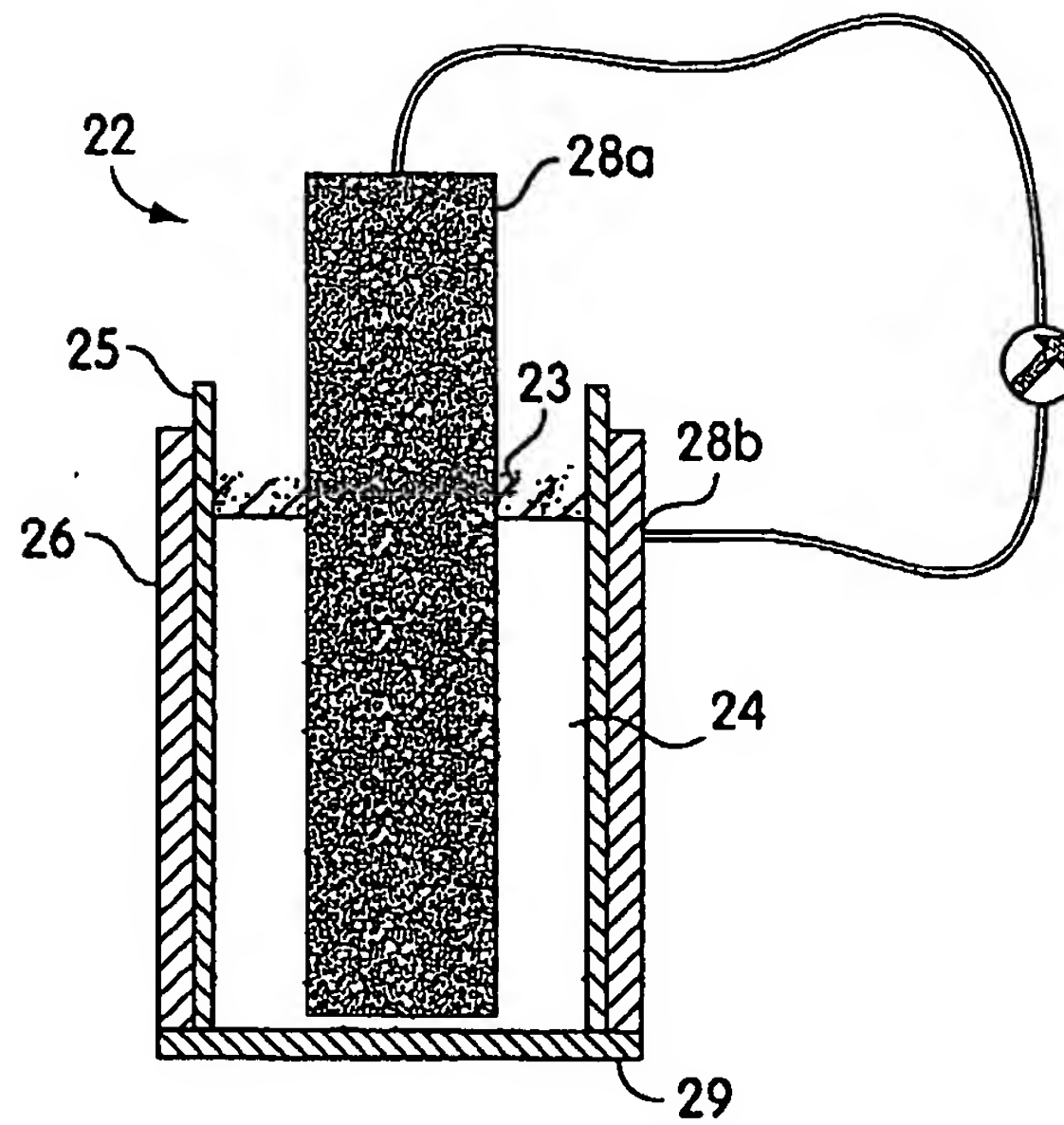


Fig. 3

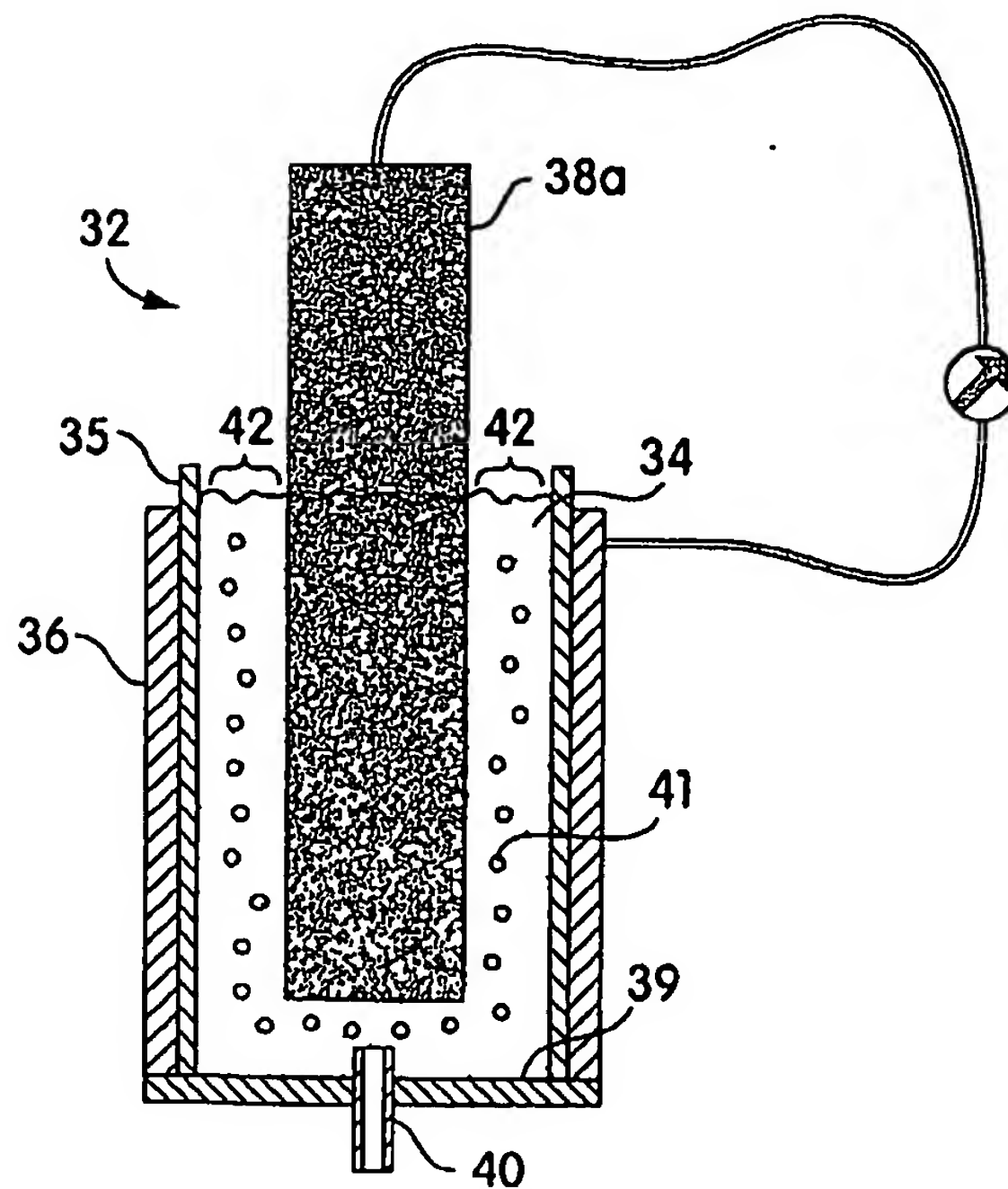


Fig. 4

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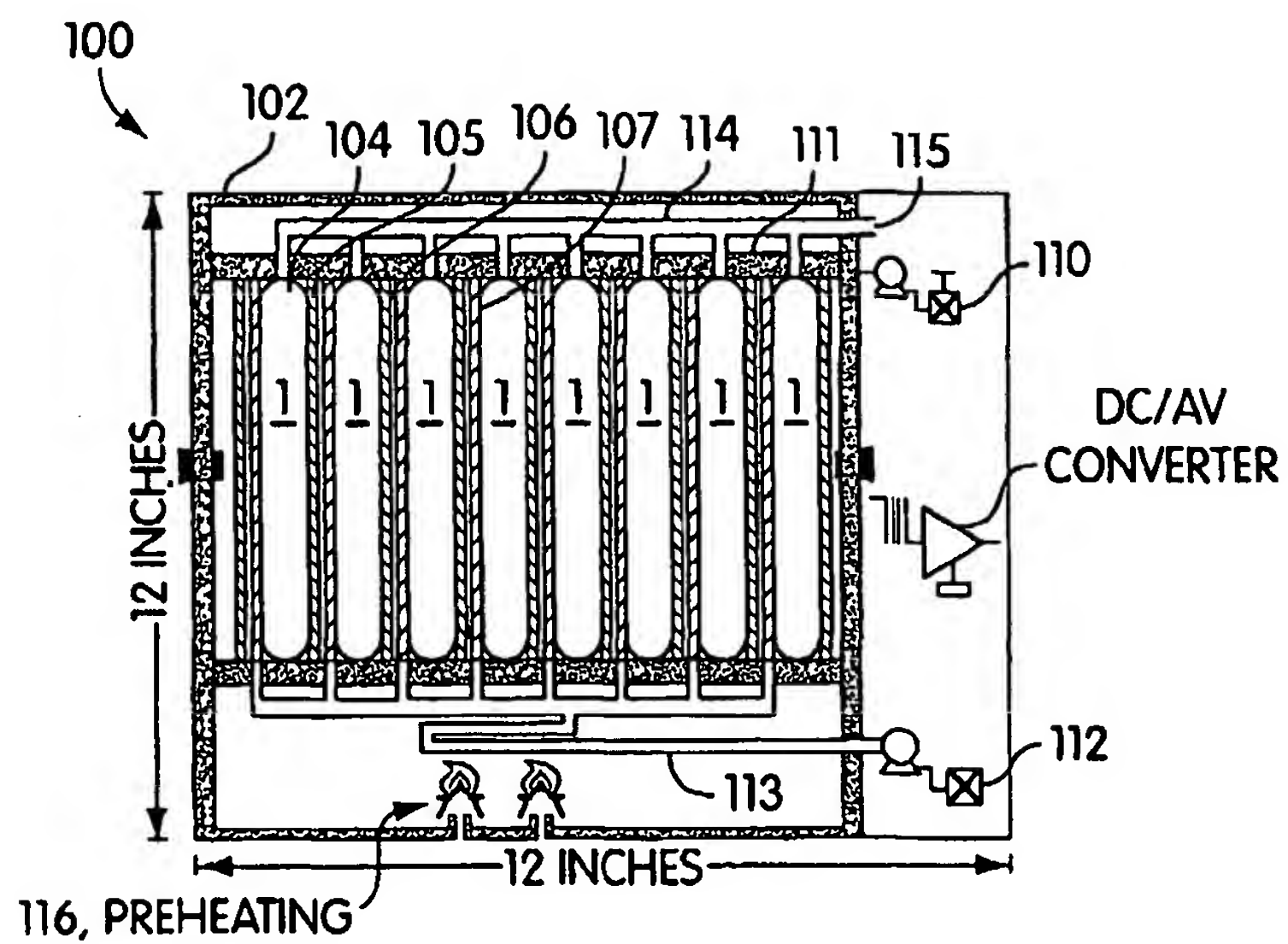


Fig. 5

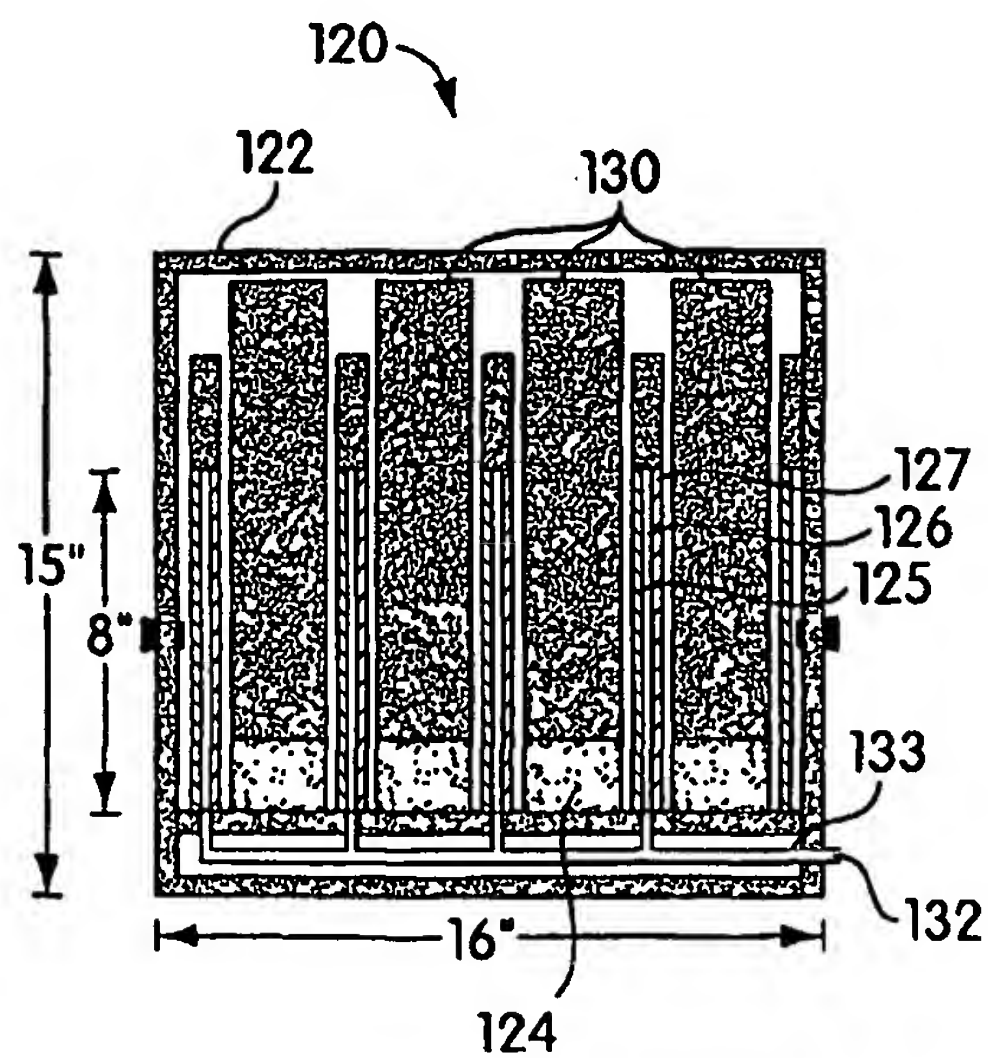


Fig. 6

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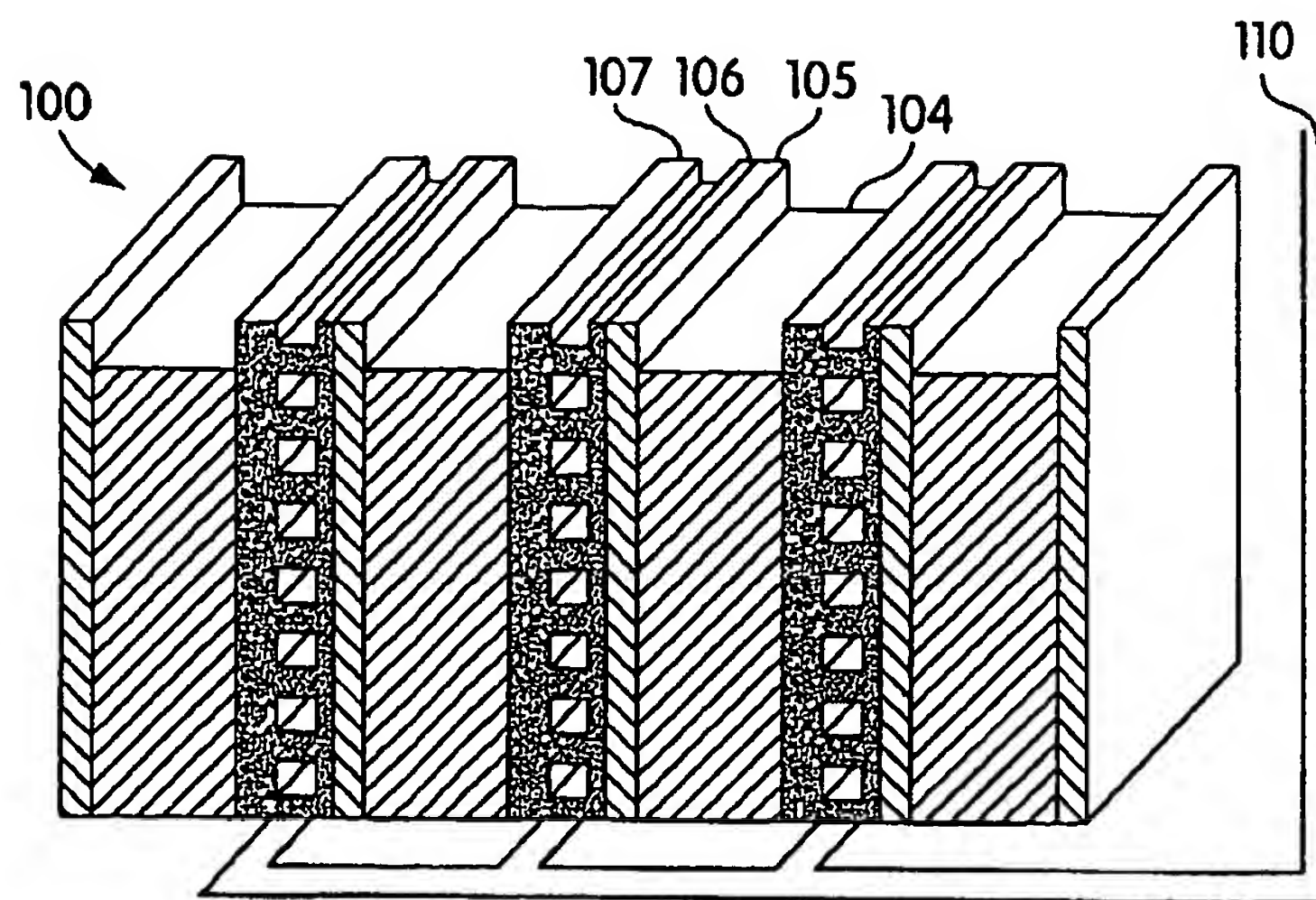


Fig. 7

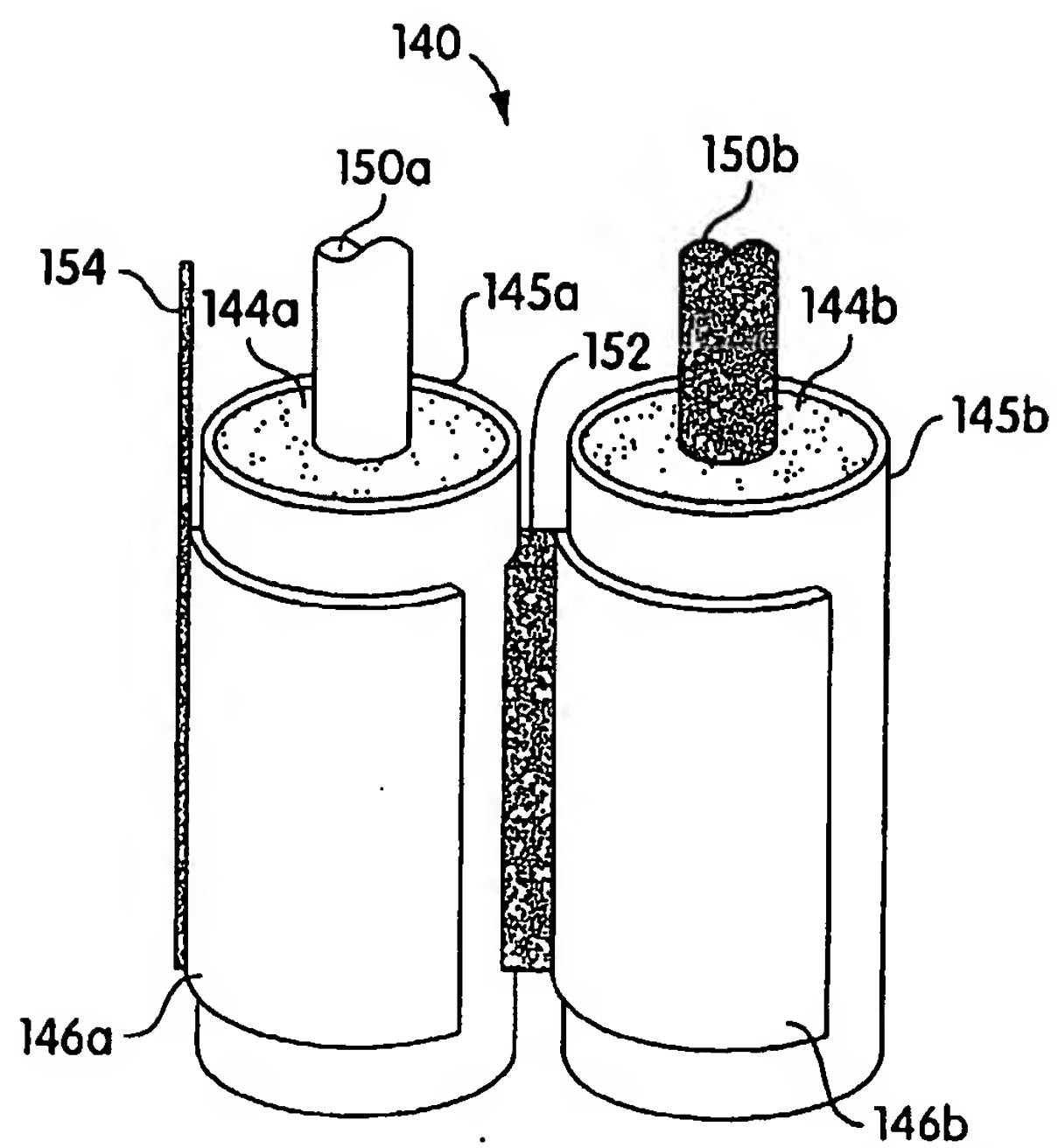


Fig. 8

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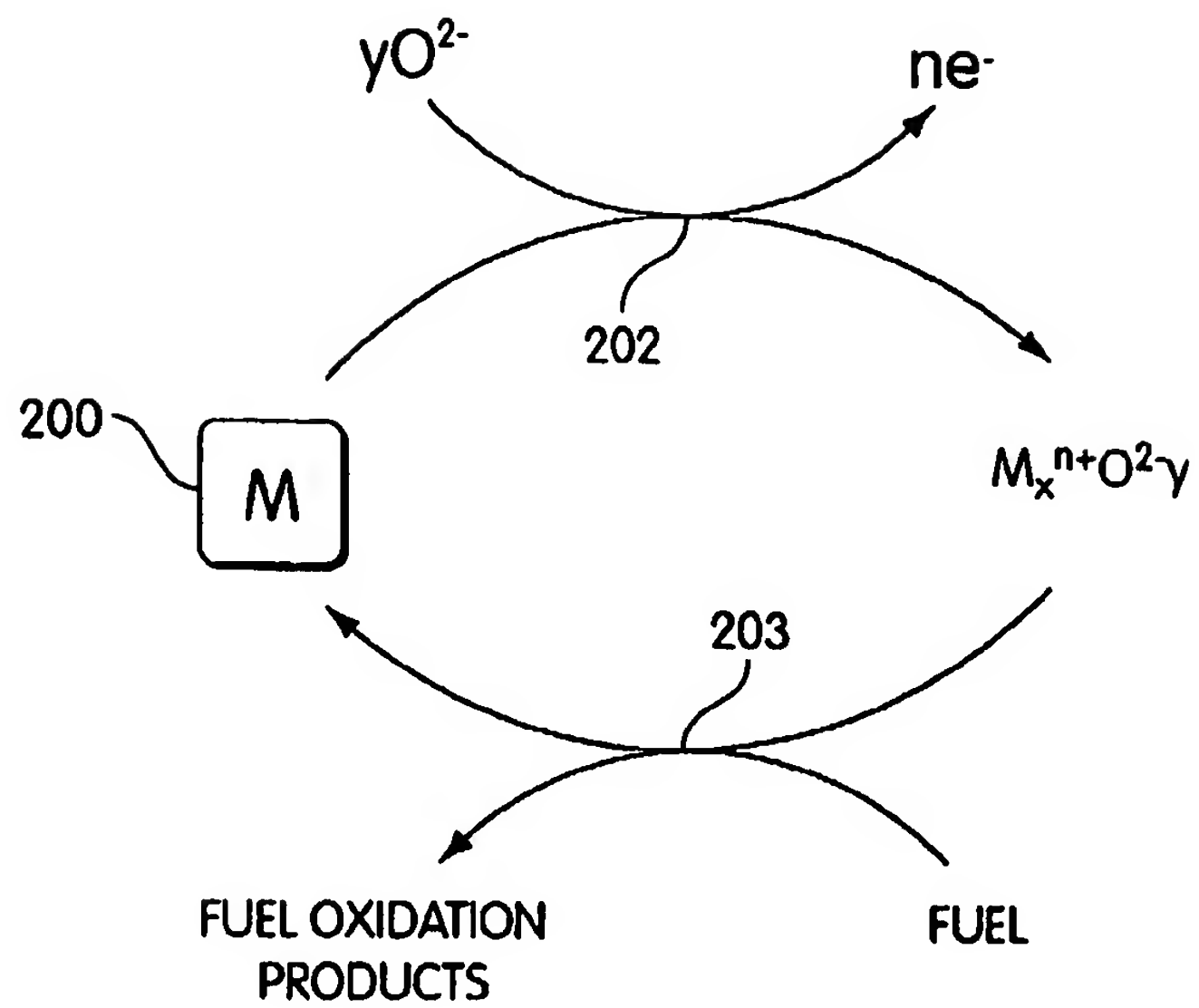


Fig. 9

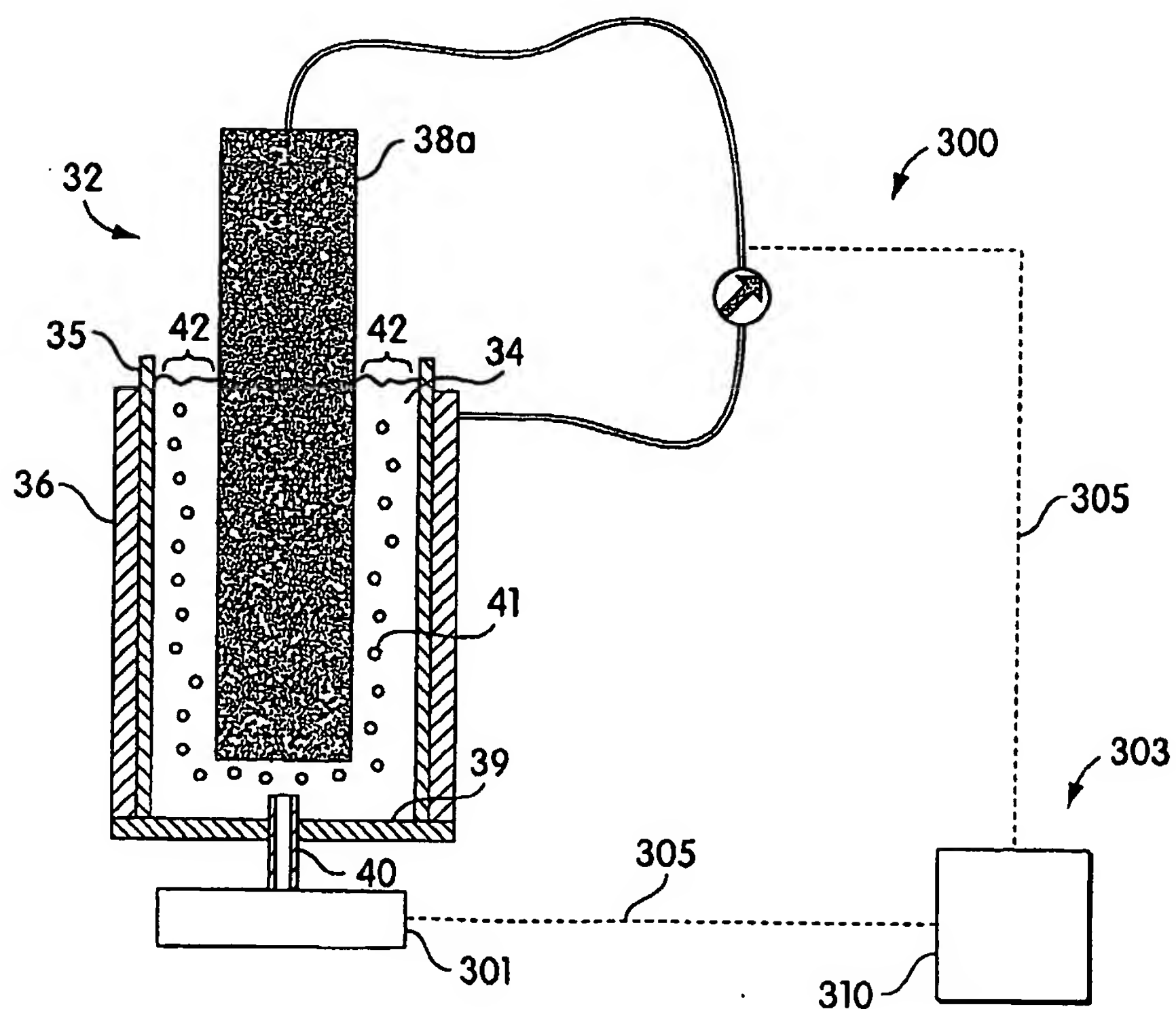


Fig. 10



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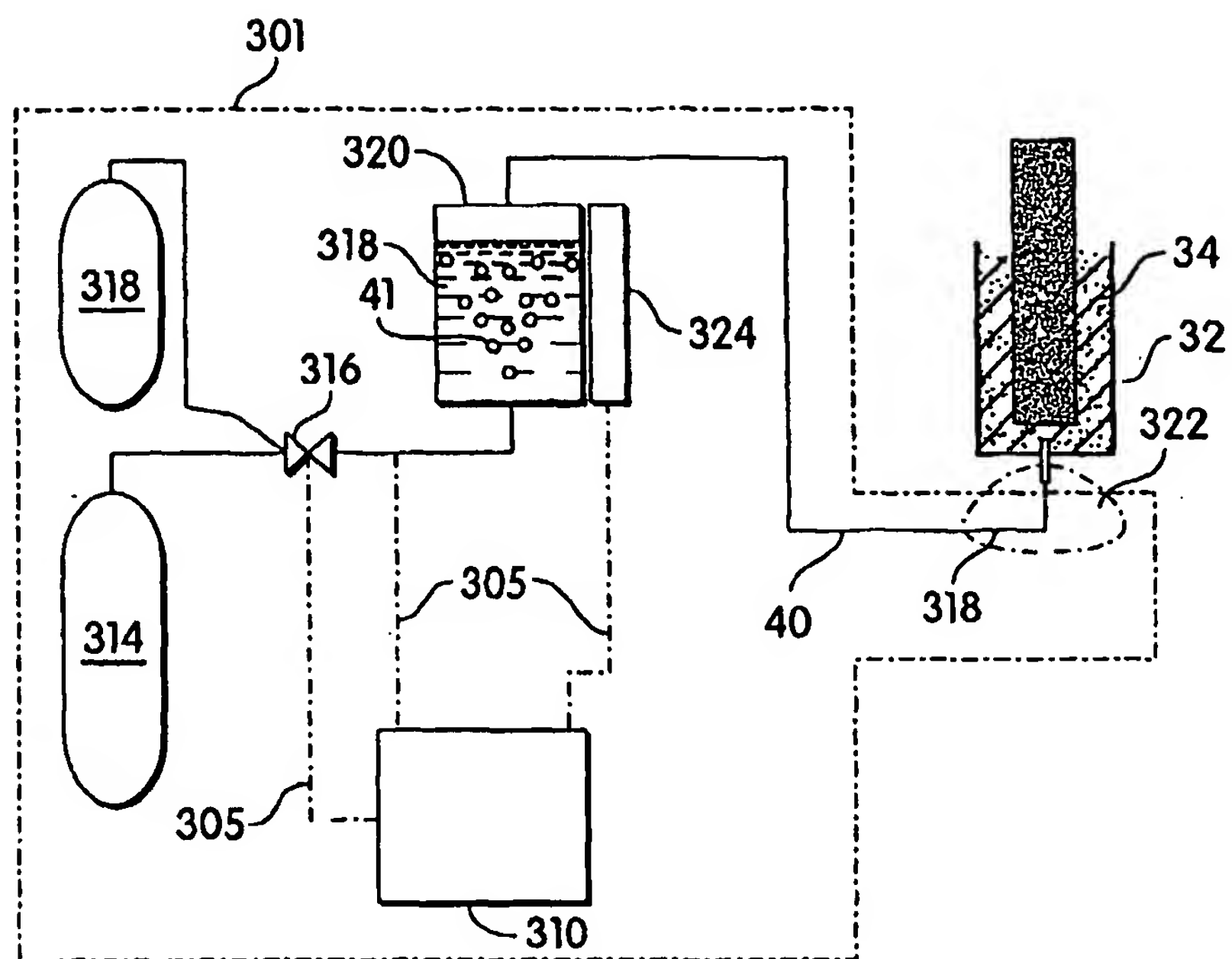


Fig. 11